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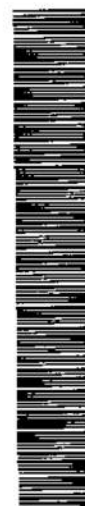


PRACTICAL TREATMENT OF COUPLED GAS EQUILIBRIUM

Max Klein
Institute for Basic Standards
National Bureau of Standards

March 1971

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FOREWORD

The research reported herein was sponsored by the Arnold Engineering Development Center (AEDC), Air Force Systems Command (AFSC), under Program Element 61102F, Task 895102, Project 8951. The work was done by the National Bureau of Standards, Washington, D. C., under Delivery Order (40-600)66-938. The manuscript was submitted for publication on January 22, 1971.

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This technical report has been reviewed and is approved.

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ABSTRACT

Equations are derived for the species concentrations in coupled chemical equilibria in the gas phase. This is done both for the method of the direct minimization of the free energy as well as for the equilibrium constant method. The relations developed are such as to allow for the inclusion of detailed real gas effects. The emphasis is on practical problems encountered in the actual calculation of the species and the thermodynamic properties. Expressions are derived for the direct calculation of the concentration derivatives with respect to temperature and density required for the calculation of the derived properties (i. e. specific heats, sound velocities, etc.). Considerable space is given to discussion of the non-linear numerical methods available for the solution of the non-linear equations for the species concentrations.

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1. INTRODUCTION

In this report we shall discuss the determination of the properties of a gaseous mixture capable of changing composition through chemical reaction. Our approach will differ somewhat from the usual textbook approach in the sense that we shall go beyond the development of the fundamental thermodynamic relations to discuss some of the practical problems which arise in the actual calculation of the thermodynamic properties and compositions for such mixtures.¹⁻⁷ We shall restrict our discussion to homogeneous gas phase reactions, the interested reader being referred to the appropriate literature for extensions which include condensed phases.⁸

In the derivations that follow, the usual assumption is made that chemical reactions can be frozen at any point in their approach to equilibrium. In other words, our system can be in thermal and mechanical but not chemical equilibrium. The reasonableness of treating such systems within the framework of thermodynamics is based essentially on the fact that the functions which describe the properties of the system when it is not in chemical equilibrium reduce to those for complete thermodynamic equilibrium on substitution of the equilibrium compositions, no other changes being required.⁹

The analysis of the chemical equilibrium problem ultimately results in a set of non-linear equations which have to be solved. Since these equations cannot be solved in closed form, numerical procedures for their solution must be developed. These numerical procedures then form an integral part of the overall solution of the problem. For this reason, a portion of this chapter has been devoted to the discussion of appropriate numerical methods.

Of primary importance in chemical equilibrium calculations is the selection of a subset of species concentrations to be a basis set (in the sense of vector analysis)² for the mathematical description of the problem. There will be a minimum number of concentrations which span the space of all species concentrations. The choice of particular species concentrations for this basis set is somewhat arbitrary. The species whose concentrations have been selected to be that set will be referred to as reference species, all other species being designated derived species. Since the number of reference species is intimately connected to the number of distinct atomic species, a certain simplicity is obtained if the atoms (and free electrons) are chosen as reference species. This particular choice of reference species is not always convenient from a computational point of view however. That problem is discussed below and simple matrix methods are presented for the transformation of species from derived to reference species and vice versa. In most of our discussion, we shall consider the gaseous mixture to consist of ℓ chemical species made up of free electrons, $c-1$ atomic species, and $m(=\ell-c)$ other species, the atomic species together with the electron being designated as reference species and all other constituents being designated derived species.

The chemical formula of any given species can be written, symbolically, as

$$S_i \equiv \prod_{j=1}^c (P_j)^{v_{ij}} \quad i = 1, \dots, l \quad (1)$$

where the P_j refer to the formulae of the reference species only (since we take these to be the atoms and free electrons). It should be noted that the reference species have also been included among the S_i . For these species, however, (1) becomes an identity, since for them $v_{ij} = \delta_{ij}$, the Kronecker delta. The subscripts v_{ij} represent the amount of reference species j contained in one molecule of species i .

A chemical reaction connecting the four species S_1 , S_2 , S_3 and S_4 can be written



According to convention, the left hand members, S_1 and S_2 are called reactants while the right hand members, S_3 and S_4 , are called products. In what follows, it will be convenient to replace the stoichiometric coefficients α_i by coefficients t_i whose magnitudes are equal to those of the corresponding α_i , but which are negative for reactants and positive for products. Equation (2) becomes

$$\sum_{i=1}^4 t_i S_i = 0 \quad (3)$$

The coefficients α_i , and hence the t_i , are chosen so that (3) is balanced for every reference species. This balancing can be simply expressed

$$\sum_{i=1}^4 t_i v_{ij} = 0 \quad (4)$$

where j runs over all the reference species.

Equation (3) has been written for the single reaction (2) involving the four species S_i . Its generalization to simultaneous chemical reactions for arbitrary numbers of species is simply

$$\sum_i t_{ik} S_i = 0 \quad (5)$$

where k runs over all the reactions and i over all species. Equation (4) is essentially unchanged by the addition of the second subscript to form t_{ik} . It will be noted that t_{ik} is zero when the i^{th} reaction does not contain the k^{th} species. In other words, the matrix \underline{T} (whose elements are the t_{ik}) is defined such that each column is associated with one species and each row with one reaction ordered in some arbitrary fashion. Each row column position of such a matrix is then associated with a particular chemical reaction, and a particular chemical species which takes part in that reaction.

The specification of the thermodynamic state of a heterogeneous mixture requires the specification of two thermodynamic variables, e.g., temperature and pressure, along with the specification of the composition of each phase. Since we shall restrict ourselves to the gas phase, it is only necessary to specify the pair of thermodynamic variables along with the composition for the single phase. The specification of the path by which this thermodynamic state was obtained is totally irrelevant to the specification of the state. For systems capable of undergoing composition change through chemical reactions, this is equivalent to stating that the particular chemical reactions by means of which the equilibrium composition was attained need not be stated. In fact, in describing any particular such state, one is free to choose any convenient set of possible reactions which includes all species of interest. The results of all discussions are then independent of such a choice. In the initial parts of what follows we shall consider all molecules and ions, which we take as the derived species, to be built up from their constituent atoms and free electrons, which we take as the reference species. This has computational advantages particularly for systems consisting of molecules containing small numbers of atoms. Practical considerations related to the numerical finiteness of computers will require the modification of this approach when the concentrations of the atomic species and electrons become extremely small. In any event, we shall always assume that each chemical reaction equation contains only one derived species, all other species in the equation being reference species which in our discussion we shall consider to be atoms and electrons.

The formation of all derived species from the reference species results in a simplification in the \underline{T} matrix. In particular, a column which refers to a derived species will contain zeros except for that one row position corresponding to the chemical reaction for the formation of that particular derived species, since that derived species cannot appear in any other reaction equation. Furthermore, this single non-zero matrix position will contain the number plus one. In what follows we shall, therefore, redefine the \underline{T} matrix to omit such columns, that is, such that only columns associated with the reference species are included, it being understood that $t_{ii} = +1$ is associated with the derived species itself. There will be no confusion on this latter point since we shall shortly explicitly insert

$t_{ij} = +1$ for the derived species in all the working relationships. An example of such a T matrix, as redefined, appears in Appendix A.

Any extensive property of a mixture can be written as a weighted sum over the corresponding partial molal quantities for each species, each such quantity being weighted by the number of moles of the species. The Gibbs free energy is such an extensive property and since the partial molal Gibbs free energy is just the chemical potential, the appropriate weighted sum takes the form

$$G = \sum_{i=1}^l n_i \mu_i \quad (6)$$

μ_i being the chemical potential and n_i the number of moles of the i^{th} species. At equilibrium, the Gibbs free energy must be a minimum with respect to all virtual variations consistent with any constraints on the system. In the absence of nuclear transformations, it is clear that any variation carried out must be such as to preserve the total number of reference species, whether bound or free. This is a constraint and leads to conservation equations which can be written in the form

$$\sum_{i=1}^l v_{ij} n_i - x_j = 0 \quad j = 1, \dots, c \quad (7)$$

For reference species other than electrons, x_j is the concentration of the j^{th} reference species, whether bound or free, in units consistent with the n_i . For the electrons, the analogous conservation equation is most conveniently expressed in terms of net charge conservation, i.e. x_j , in this case, represents the net overall charge of the gas. In particular, for a neutral gas, $x_j = 0$.

The problem with which we shall be occupied can thus be stated as being the determination of the composition variables n_i , such that the free energy given by (6) is a minimum under all virtual variations, subject to the constraints (7). There have developed two numerical approaches to the solution of this problem. In one of these, the problem is numerically attacked directly as stated and, in fact, composition variables are sought which result in a stationary value of G , subject to the stated constraints. This method is referred to as the direct minimization of the free energy. In the second approach, the formalism is allowed to proceed further before the numerical attack is mounted. Thus, formal variation of (6) is carried out, subject to the constraints (7). There results a series of equations each of which connects composition variables with the composition independent parts of the chemical potentials for those species appearing

in the equation. Since these composition independent terms can be combined to define an equilibrium constant, this second method is referred to as the equilibrium constant method. We shall now proceed to derive the working equations for the two methods. In what follows, we shall formally carry along in the derivation terms containing various departures from the ideal gas. Having derived the required relations, we shall then specialize them to the ideal gas in discussing methods for solution. The detailed way in which the non-idealities are calculated is contained in Appendix B. Modifications in the methods of solution as required by these non-idealities will be indicated but not discussed in detail.

2. DIRECT MINIMIZATION OF THE FREE ENERGY^{3,5,6,11}

In principle, the equations associated with this method have been derived, namely, (6) and (7). For an ideal gas, these can be written more explicitly in terms of the mole fractions of the species. Thus, the chemical potential for a constituent in a mixture can be written

$$\frac{\mu_i(T,P)}{RT} = \frac{\mu_i^*(T,P)}{RT} + \ln x_i + \ln \gamma_i \quad (8)$$

where x_i is the mole fraction of the species in the mixture, $\mu_i^*(T, P)$ the chemical potential of the pure species i at the same temperature and pressure, and γ_i the activity coefficient of species i in the solution. γ_i contains all departures from ideality. For a real gas, γ_i depends on T, P , and the concentrations of the various constituents. For an ideal gas $\gamma_i = 1$, in which case the concentration dependence reduces simply to the natural logarithm of the mole fraction. μ_i^* can, of course, be written

$$\frac{\mu_i^*(T,P)}{RT} = \frac{\mu_i^0(T)}{RT} + \ln P \quad (9)$$

in which the standard state is taken as 1 atm. (101325.0 N/m^2) and where $\mu_i^0(T)$ depends only on the temperature. In what follows, it will be convenient to write the free energy, G , in dimensionless form by dividing it by RT . Substitution of (8) into the dimensionless form of (6) then yields

$$\frac{G}{RT} = \sum_{i=1}^L n_i \left[\frac{\mu_i^*}{RT} + \ln \left(\frac{n_i}{\sum n_i} \right) + \ln \gamma_i \right] \quad (10)$$

The chemical equilibrium problem is then solved, by the method of the direct minimization of the free energy, when the set of composition variable n_i is found which minimizes (10) subject to the c equations (7) being satisfied. It should be noted that when real gas effects are included, the γ_i can depend on the concentrations of all species. This will complicate certain of the numerical methods used in the solution for the direct minimization of the free energy.¹²

3. THE EQUILIBRIUM CONSTANT METHOD

As we have already stated, this method starts with the formal variation of (6) subject to (7). The fact that the n_i appear in both (6) and (7) indicates that the formal variation of the n_i in (6) cannot be carried out independently. These variations can be made independent by the elimination of the proper number of variables. This can be accomplished by the method of Lagrange multipliers¹³ in which a sum over the c equations (7), each multiplied by an unknown multiplier λ_j , is added to (6). When this is done and the variation carried out, there results

$$\begin{aligned} \delta G = & \sum_{i=1}^{\ell} \left(\mu_i + \sum_{j=1}^c \lambda_j v_{ij} \right) \delta n_i \\ & + \sum_{j=1}^c \left(\sum_{i=1}^{\ell} v_{ij} n_i - x_j \right) \delta \lambda_j \end{aligned} \quad (11)$$

where the unknown Lagrange multipliers λ_j are defined so as to eliminate the proper number of coefficients of the δn_i . All remaining variations then become independent. The two sets of variations in (11) can then be carried out independently. This leads to the set of equations

$$\mu_i + \sum_{j=1}^c \lambda_j v_{ij} = 0 \quad i = 1, \dots, \ell$$

$$\text{and} \quad \sum_{i=1}^{\ell} v_{ij} n_i - x_j = 0 \quad j = 1, \dots, c$$

The first of these can be used to evaluate the Lagrangian multipliers λ_j and

to determine their meaning. Since $\mu_i = -\sum_j \lambda_j v_{ij}$, it follows from (6) that

$$G = \sum_i \mu_i n_i = - \sum_{i,j} \lambda_j v_{ij} n_i$$

But, from the second set of relations above

$$\sum_i v_{ij} n_i = x_j$$

so that

$$G = - \sum_j \lambda_j x_j$$

and $-\lambda_j$ can be considered to be the contribution of reference species j (whether bound or free) to the free energy. Since

$$-\lambda_j = \left(\frac{\partial G}{\partial x_j} \right)_{T,P,x_1, \dots, x_{l+j}}$$

it follows that $-\lambda_j$ is, in effect, the chemical potential of the reference species whether bound or free.

Equation (11) contains the l variations δn_i . The fact that these are subject to the c constraints (7), means that there must exist $l-c$ variables which can be varied independently. This is equivalent to the statement that there exists at least one set of $l-c$ chemical reactions for the attainment of the thermodynamic state. One such set of reactions can be obtained by considering each derived species to be a product and requiring it to be built up from its constituent reference species, the latter considered to be reactants. One obtains, thereby, $l-c$ chemical reactions for the derived species (along with c superfluous identity chemical reactions for the reference species). Clearly any other set of reactions containing more than $l-c$ reactions must contain redundancies.

Having reduced the number of reactions to $l-c$, one can obtain an equal

number of variables by defining a variable to go with each reaction. This is the sense of de Donder's¹⁴ introduction of the degree of reaction variable. This variable is defined in terms of the change in the number of moles of a species produced by a particular chemical reaction. Thus, the change in the number of moles of species j as a result of the i^{th} reaction is given by

$$(\delta n_j)_i = t_{ji} (\delta \xi_i)$$

where ξ_i is the degree of reaction of chemical reaction i . By definition, the same value of $\delta \xi_i$ must apply to each species in the i^{th} reaction, the scale for each such species being given by t_{ji} . The total change in the number of moles of the j^{th} species for the mixture can be calculated by summing these changes over all reactions. This yields

$$\delta n_j = \sum_i t_{ji} \delta \xi_i \quad (12)$$

which can be used in (11) to demonstrate the independence of the variations $\delta \xi_i$. Thus, substitution of (12) in (11) yields

$$\begin{aligned} \delta G &= \sum_{i=1}^L (\mu_i + \sum_{j=1}^C \lambda_j v_{ij}) \sum_{k=1}^L t_{ik} \delta \xi_k \\ &+ \sum_{j=1}^C \left(\sum_{i=1}^L v_{ij} n_i - x_j \right) \delta \lambda_j = 0 \\ &= \sum_{i,k} \mu_i t_{ik} \delta \xi_k + \sum_{i,j,k} \lambda_j v_{ij} t_{ik} \delta \xi_k + \sum_{j=1}^C \left(\sum_{i=1}^L v_{ij} n_i - x_j \right) \delta \lambda_j \end{aligned}$$

But, according to the generalized form of (4),

$$\sum_i v_{ij} t_{ik} = 0$$

so that

$$\delta G = \sum_{i,k} \mu_i t_{ik} \delta \xi_k + \sum_{j=1}^c \left(\sum_i v_{ij} n_j - x_j \right) \delta \lambda_j = 0$$

The fact that the λ_j have disappeared from the first term on the right means that the variations have been uncoupled. Independent variation of the terms in this last equation then leads to the relation

$$\sum_i \mu_i t_{ij} = 0 \quad j = 1, \dots, l-c \quad (13)$$

(the so-called equations of reaction equilibrium) as well as the c equations (7). The $l-c$ equations (13) along with the c relations (7) also completely specify the system. Equations (13) will form the basis for the derivation of the working equations of the equilibrium constant method.

Let us again consider the derived species to be formed only from reference species. As previously mentioned, for such chemical reactions the coefficient of the derived species must be plus unity so that (13) can be written

$$\mu_i + \sum_{j=1}^c \mu_j t_{ij} = 0 \quad i = 1, \dots, l-c \quad (14)$$

where i now refers only to derived species and j refers only to reference species and where there no longer remains the possibility for confusion with regard to the removal from the T matrix of the columns corresponding to the derived species.

Equations (14) are valid for all values of temperature and pressure for which the system is in thermodynamic equilibrium. The explicit dependence of these equations on composition for the ideal gas becomes clear on the substitution of (9) into (8), setting $\gamma_i = 1$, and substituting the result

into (14). We choose, however, to carry along the activity coefficient for the present. (14) then becomes

$$\frac{\mu_i^0}{RT} + \sum_j t_{ij} \frac{\mu_j^0}{RT} + \ln P + \sum_j t_{ij} \ln P + \ln x_i + \sum_j t_{ij} \ln x_j + \ln \gamma_i + \sum_j t_{ij} \ln \gamma_j = 0 \quad (15)$$

The first two terms depend only on the temperature. It is customary to combine such terms into an equilibrium constant K_i for the i^{th} reaction (and hence for the i^{th} derived species) by the definition

$$- \ln K_i = \frac{\mu_i^0}{RT} + \sum_j t_{ij} \frac{\mu_j^0}{RT} \quad (16)$$

Substitution into (15) leads to

$$- \ln K_i + \ln P^{(\sum t_{ij} + 1)} + \ln x_i + \sum_j t_{ij} \ln x_j + \ln \gamma_i + \sum_j t_{ij} \ln \gamma_j = 0$$

which can be written

$$K_i = \left[\prod_j \gamma_j^{t_{ij}} \right] \gamma_i \cdot P^{-\omega_i} \left[\prod_j x_j^{t_{ij}} \right] x_i \quad (17)$$

where $\omega_i = [\sum t_{ij} + 1]$ is the increase in the number of particles in the reaction in going from derived to reference species. In what follows it will be convenient to introduce an activity coefficient for the reaction by defining

$$\gamma_i' = \left[\prod_j \gamma_j^{-t_{ij}} \right] / \gamma_i$$

(17) can then be written

$$K_i \gamma_i' = P^{-\omega_i} \left[\prod_j x_j^{t_{ij}} \right] x_i \quad (17a)$$

We shall now restrict ourselves to the ideal gas, taking $\gamma_i = 1$ as required. Real gas effects can be included through the introduction of explicit expressions for γ_i' as described in the appendix.

For the ideal gas, (17) can be rewritten so that the mole fraction of the derived species appears on the left and only reference species appear on the right. Thus, by transposition (17) becomes, for $\gamma_i' = 1$

$$x_i = K_i P^{\omega_i} \prod_j x_j^{-t_{ij}} \quad (17b)$$

Since, for reactants $t_{ij} = -v_{ij}$, (17b) can now be simply written in terms of the stoichiometric coefficients, i.e.

$$x_i = K_i P^{\omega_i} \prod_j x_j^{v_{ij}} \quad (18)$$

while the activity coefficient for the reaction becomes

$$\gamma_i' = \left[\prod_j \gamma_j^{v_{ij}} \right] / \gamma_i$$

Equation (18) will form the basis for computations within the framework

of the equilibrium constant method. Because we have chosen to write the chemical reactions entirely in terms of atoms and the electron as reference species, (18) contains v_{ij} in an unambiguous manner with regard to sign. In what follows, we shall also continue to use t_{ij} on occasion in order to maintain complete generality.

Equation (18) is appropriate for calculations in which pressure is a thermodynamic state variable. If, for some reason, partial pressures are preferred over mole fractions, use can be made of the definition $P_j = x_j P$ where P_j is the partial pressure and (18) is then written

$$P_i = K_i \prod_j P_j^{v_{ij}}$$

Quite often density is a more convenient state variable than pressure. Conversion of (18) to the corresponding density form requires the explicit use of the equation of state which connects pressure and density. Thus since P is expressed in bars (or atmospheres), this can be written

$$x_i = K_i (P/P_0)^{\omega_i} \prod_j x_j^{v_{ij}}$$

where P_0 is understood to refer to the pressure at specified reference conditions (usually $T = 273.15$ K and $P = 1$ bar (or 1 atm.)). The equation of state can be written $P = \rho ZRT$ where Z is the compressibility factor. For the one component ideal gas, Z is unity with departures from unity being due entirely to non-ideality. We shall use the same form for the equation of state for the reacting multicomponent gas. In that case, it is convenient to let $1/\rho$ be the volume per mole of the reaction mixture so that, for the ideal gas, Z becomes the number of moles, a quantity which depends on the thermodynamic state parameters. Naturally, for the multicomponent real gas, Z also contains the effect of non-ideality. Now, the equations of state are $P = \rho ZRT$ for the conditions of interest and $P_0 = \rho_0 Z_0 RT_0$ at the reference state so that

$$\frac{P}{P_0} = \frac{\rho}{\rho_0} \frac{Z}{Z_0} \frac{T}{T_0}$$

(18) can then be written

$$C_i = K_i \left(\frac{T}{T_0} \right)^{w_i} \left(\frac{\rho}{\rho_0} \right)^{w_i} \prod_j C_j^{v_{ij}}$$

where $C_i = x_i Z/Z_0$ is the concentration of species j in moles per mole of equilibrated gas at the reference conditions. It should be noted that the reference state is being used for purposes of scaling all results and not as a standard state in the usual chemical sense. The use of this particular reference state may be inconvenient in some systems in which case, if solutions are still desired at specified densities, either other definitions of the variables subscripted zero should be used or calculations at the desired densities carried out in a pressure formulation for which no such reference state is needed with an iteration inserted so that the particular pressure which corresponds to the desired density is determined.

Since, in what follows a reference state will always be used for scaling, the dropping of the Z should result in no confusion. With this in mind, Z/Z_0 can be replaced by Z and the concentrations defined $C_i = x_i Z$, it being understood that these are with respect to one mole in the reference state.

It is convenient to combine the factors which depend only on temperature by defining an equilibrium constant

$$\bar{K}_i = K_i \left(\frac{T}{T_0} \right)^{w_i}$$

One obtains, thereby,

$$C_i = \bar{K}_i (\rho/\rho_0)^{w_i} \prod_j C_j^{v_{ij}} \quad (19)$$

For consistency (7) should be expressed in the same units as (19). Thus (7) becomes

$$\sum_{i=1}^L v_{ij} C_i - x_j = 0 \quad j = 1, \dots, c \quad (20)$$

where x_j is now in moles per mole of gas at the reference state. Since, for the electrons, (20) represents the net charge conservation equation (with positive and negative charges balancing each other), for them v_{ij} in (20) is replaced by t_{ij} .

Equations (19) and (20) are the working equations for the equilibrium constant method. These equations constitute a set of l equations for the concentrations of all of the species, (i.e. both the reference and derived species). As mentioned earlier, these l concentrations are completely determined once the concentrations of the c reference species have been specified. The problem can be viewed, therefore, as requiring the solution of the c simultaneous equations (20) subject to the l - c conditions (19). The meaning of this view of the problem will become somewhat more transparent when expressions are derived below for the calculation of the derivatives of the concentrations. The validity of this view can be demonstrated on substituting (19) into (20). This yields the set of equations

$$\sum_{i=1}^l v_{ij} \bar{K}_i \left(\frac{p}{p_0} \right)^{\omega_i} \prod_{j=1}^c x_j^{v_{ij}} - x_j = 0 \quad j = 1, \dots, c \quad (21)$$

which is a set of c equations in c unknowns, i.e. the c reference species.

Equations (21) are a set of highly nonlinear equations. The nonlinearity arises both from the exponents v_{ij} on the unknown variables as well as from the appearance of products of the unknowns. The question of the existence of multiple solutions naturally arises in such cases. Such problems are beyond the scope of this report. The interested reader is referred to recent literature¹⁵ addressed to this problem.

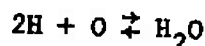
We have now obtained the working equations for the two approaches to the problem. These are (7) and (10) for the free energy minimization method and (19) and (20) for the equilibrium constant method. Both methods require as input the chemical potentials of the individual chemical species (see equations (10) and (16)). In the ideal gas limit appropriate to our calculations, these and other thermodynamic properties of the individual species can, in principle, be simply calculated by summation over the species energy levels.¹⁶ In practice, there can be problems, however, as we shall mention below.

4. TRANSFORMATIONS AMONG SETS OF REFERENCE SPECIES

Either of the two sets of equations obtained, i.e. (7) and (10) or (19) and (20) can, in principle, be solved for the concentrations of the various constituents in the mixture. These equations contain the assumption that there is available a complete specification of the system for input, i.e. the temperature and density of the mixture, the thermodynamic properties of the constituents, and the specification of the mixture itself (through the

values assigned to the χ_i). We have formally assumed that all derived species are obtained directly from the chemical combining of the atomic species. Because of this, the solution is specified in terms of the concentrations of these atomic species. This will become somewhat clearer below. As mentioned earlier, the specification of a precise set of chemical reactions from which the species are derived is irrelevant to the specification of the thermodynamic state of the system. The particularization of the reactions is needed only for converting the thermodynamic formalism into a computational structure. It follows, therefore, that changing from one set of reactions to another produces no fundamental thermodynamic changes in any of the results obtained.

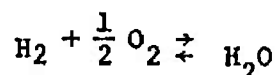
Now a particular set of chemical reactions will be convenient, from a computational point of view, for only a limited set of thermodynamic conditions. Thus, for example, for chemical reactions in the system H_2O , H_2 , O_2 , H , and O , the use of the atomic species H and O as reference species, while thermodynamically correct, will not be convenient from a computational point of view at temperatures sufficiently low that little dissociation occurs. While equation (19) in terms of atomic reference species is correct for the reaction



under all conditions, computational difficulties occur at low temperatures where the concentrations of the atomic species, $C_{1,2}$, become extremely small and where the equilibrium constants K_1 (and hence K_2) become extremely large.

Despite the fact that the C_i obtained for H_2O at low temperatures by solving (19) must be of reasonable magnitude, it is possible, in the process of carrying out the multiplications required in the right hand side of (19), for numbers to be produced whose magnitudes are outside the limits set by the computer design. This can often be avoided by changing the order of multiplication so that small numbers like the C_i alternately multiply large ones like K_1 or by taking logarithms. A second problem is associated with the magnitude of K_1 . While this too is a soluble problem, solutions are always artificial (e.g., by representing K_1 as a product of factors).

A much more reasonable and more physical way to solve both these problems exists, namely the replacing of the arbitrarily chosen set of chemical reactions used by another set from which reference species can be defined whose magnitudes are within the limits set by the computer. For example, at low temperatures it is obvious that H_2O should be formed from molecular oxygen and molecular hydrogen. That is, the computational framework should be based on H_2 and O_2 as reference species with the H_2O reaction becoming



It should be noted that the coefficient of the derived species has been kept

equal to unity to be consistent with the definition of the \underline{T} matrix.

In this section we shall indicate how such transformations of reference species may be carried out. We shall merely describe how the elements of the \underline{T} matrix are to be changes, the details required to make the transformation part of a computational program being left to the interested reader.

Equation (14) can be written

$$\mu_i = -\sum_{j=1}^c t_{ij} \mu_j \quad i = 1, \dots, l \quad (22a)$$

where j refers to the reference species and i to the derived species. Equations (22a) include the c identity equations for the reference species since these also undergo transformation. In matrix notation (22a) can be written

$$\vec{\mu}' = -\underline{T} \cdot \vec{\mu} \quad (22b)$$

with $\vec{\mu}'$ an l element column vector and $\vec{\mu}$ a c element row vector. \underline{T} is, of course an l element row by a c element column matrix.

In carrying out a transformation of reference species, it is essential that the number of final reference species be the same as the number of original reference species. In Brinkley's terminology² this requires that the dimension of the vector space (i.e. the rank of the \underline{T} matrix) be invariant under the transformation. This requires the equations connecting the new reference species with the old to contain as many equations as unknowns, i.e. the matrix associated with the transformation must be square. In other words, if double primes refer to the new reference species, there is a subset of equations (22a) which can be written

$$\mu_j'' = -\sum_{k=1}^c t_{kj} \mu_k \quad j = 1, \dots, c$$

where the t_{kj} are now the elements of a square matrix. This can also be written in the vector notation of (22b). Thus

$$\vec{\mu}'' = -\underline{T}_s \cdot \vec{\mu} \quad (22c)$$

where the subscript s is meant to indicate the square matrix associated with the two sets of reference species. Since T_s is square, (22c) can formally be solved for $\vec{\mu}$ in terms of $\vec{\mu}''$ by multiplying by T_s^{-1} from the left. There results

$$T_s^{-1} \cdot \vec{\mu}'' = -\vec{\mu} \quad (22d)$$

(22b) can now be written in terms of the new reference species by substituting (22d) for $\vec{\mu}$ in (22b). There results

$$\vec{\mu}' = T \cdot T_s^{-1} \cdot \vec{\mu}'' = T_1 \cdot \vec{\mu}''$$

with the elements of T_1 constituting the new coefficient matrix. It should be noted that the elements associated with the previous reference species will no longer be Kronecker deltas, whereas those associated with the new reference species will become Kronecker deltas. As will become clear below, these transformations must be accompanied with various changes in the identities of rows and columns in the original T matrix.

The transformation is not complete until the constants χ_j have been transformed to those appropriate to the new reference species. In matrix form, (20) can be written

$$\vec{C} \cdot T = \vec{\chi}$$

Multiplication by the square array T_s^{-1} from the right yields

$$\vec{C} \cdot T \cdot T_s^{-1} = \vec{\chi} \cdot T_s^{-1}$$

But $T \cdot T_s^{-1} = T_1$ so that this becomes

$$\vec{C} \cdot T_1 = \vec{\chi} \cdot T_s^{-1}$$

and it is clear that the transformations of the χ_j constitute the elements of the vector equation

$$\vec{X}' = \vec{X} \cdot \underline{T}_S^{-1}$$

In order to clarify the mechanics of the transformation, let us take, as an example, the set of reactions among the species CO_2 , CO , O_2 , C , and O . When the atoms C and O are taken as reference species, the elements of the \underline{T} matrix are given by

$$\begin{array}{c} \text{CO}_2 \\ \text{CO} \\ \text{O}_2 \\ \text{C} \\ \text{O} \end{array} \begin{array}{c} \text{C} \quad \text{O} \\ \left(\begin{array}{cc} 1 & 2 \\ 1 & 1 \\ 0 & 2 \\ 1 & 0 \\ 0 & 1 \end{array} \right) \end{array}$$

Suppose, now, that it is desired to transform to CO and O_2 as reference species. The transformation matrix \underline{T}_S and its inverse are easily seen to be given by

$$\underline{T}_S = \begin{array}{c} \text{CO} \quad \text{O}_2 \\ \text{C} \quad \left(\begin{array}{cc} 1 & 0 \\ 1 & 2 \end{array} \right) \\ \text{O} \end{array} ; \quad \underline{T}_S^{-1} = \begin{pmatrix} 1 & -\frac{1}{2} \\ 0 & \frac{1}{2} \end{pmatrix}$$

with the new matrix \underline{T}_1 calculated from

$$\underline{T}_1 = \underline{T} \cdot \underline{T}_S^{-1} = \begin{array}{c} \text{CO}_2 \\ \text{CO} \\ \text{O}_2 \\ \text{C} \\ \text{O} \end{array} \begin{pmatrix} 1 & 2 \\ 1 & 1 \\ 0 & 2 \\ 1 & 0 \\ 0 & 1 \end{pmatrix} \begin{pmatrix} 1 & -\frac{1}{2} \\ 0 & \frac{1}{2} \end{pmatrix} = \begin{array}{c} \text{CO}_2 \\ \text{CO} \\ \text{O}_2 \\ \text{C} \\ \text{O} \end{array} \begin{array}{c} \text{CO} \quad \text{O}_2 \\ \left(\begin{array}{cc} 1 & \frac{1}{2} \\ \frac{1}{2} & 0 \\ 0 & 1 \\ \frac{1}{2} & -\frac{1}{2} \\ 0 & \frac{1}{2} \end{array} \right) \end{array}$$

where the shift of reference species is indicated by a shift in the location of the diagonal unit submatrix between the dashed lines.

To illustrate the transformation on the χ_1 , suppose there to be 1 mole of CO_2 present so that, for C and O as reference species, $\chi_1 = 1$, $\chi_2 = 2$. Thus

$$\vec{\chi}' = (1 \quad 2) \begin{pmatrix} 1 & -\frac{1}{2} \\ 0 & \frac{1}{2} \end{pmatrix} = \begin{pmatrix} \frac{1}{2} \\ \frac{1}{2} \end{pmatrix}$$

and, for CO and O_2 as reference species, the values $\chi_1 = 1$, $\chi_2 = \frac{1}{2}$ are appropriate.

Clearly transformations of this kind can be carried out automatically within the framework of any computer program designed to solve the equations for the concentrations. We shall not describe how this might be done in practice. A word of caution is in order, however, and that is that, as should become clear in the next section, since the reference species are changed, these transformations must always be accompanied with a shift in the energy differences (i.e. heats of reaction) used to produce derived species from reference species.

5. SOME PROBLEMS IN THE CALCULATION OF IDEAL GAS FUNCTIONS FOR THE INDIVIDUAL SPECIES

The only microscopic information that has thus far been included in the formalism is contained in (1) and is merely the labeling of each derived species in terms of its constituent reference species. The points of entry for the detailed microscopic properties of individual constituents have already been passed. These are (10) for the free energy minimization method and (16) for the equilibrium constant method. For a pure component, the chemical potential is the same as the free energy per mole so that in (9)

$$\frac{\mu(T)}{RT} = \frac{(G_T^0 - E_O^0)}{RT} + \frac{E_O^0}{RT}$$

where G_T^0 is the ideal gas Gibbs free energy for the species and (E_O^0) is the reference energy at zero kelvin. The expression for the equilibrium constant (16), becomes

$$\ln K_1 = - \frac{(G_T^\circ - E_0^\circ)_i}{RT} + \sum_j \nu_{ij} \frac{(G_T^\circ - E_0^\circ)_j}{RT} - \frac{(E_0^\circ)_i}{RT} + \sum_j \nu_{ij} \frac{(E_0^\circ)_j}{RT}$$

Both methods, therefore, require the ideal gas Gibbs function relative to the energy of a reference state, E_0° for the individual species.

Since only energy differences have physical meaning, the choice of E_0° values would appear to be entirely arbitrary. In a reacting system, however, the difference between E_0° for reactant and products is physically meaningful and is, in fact, the reaction energy $\Delta E_0^\circ/RT = \frac{(E_0^\circ)_i}{RT} - \sum_j \nu_{ij} \frac{(E_0^\circ)_j}{RT}$

at absolute zero. For this reason, the choice must be made in a manner which is consistent among species. In most cases, taking E_0° to be zero for the reference species avoids complications. Of course, all choices are valid provided only that they are consistent. It should perhaps be pointed out again that whatever reference point is taken for the energy must be examined carefully after any transformation to new reference species is carried out.

The quantity $(G_T^\circ - E_0^\circ)/RT$ can be calculated for each species using statistical mechanics and the details of the internal structure of that species. The Gibbs free energy for an ideal gas species is related to the partition function through the relation

$$\frac{(G_T^\circ - E_0^\circ)}{RT} = - \ln Q$$

where Q is the ideal gas partition function. Q contains translational and electronic contributions for all species (except for the electrons for which only a translational part is appropriate). For molecular species there are additional contributions from vibrational and rotational energies. A discussion of methods for the evaluation of such partition functions is outside the scope of this report and the interested reader is referred elsewhere¹⁶ for such details. In this report, we assume that the Gibbs free energies have been calculated properly and are available as input to the calculation. We shall, however, mention some problems associated with the evaluation of the partition functions since such problems are not always described in the literature.

Perhaps the most serious such problem has to do with the actual divergence of these partition functions. There are an infinite number of energy levels just below the ionization limit of an atom. These terms, if included

in the summation, would cause the partition function to diverge. At moderate temperatures, which can be as high as several thousand kelvins this causes no trouble since the contribution of successive energy levels, starting from the lowest, tends to drop off rapidly and goes through a broad minimum starting with a relatively small quantum number. The series can therefore be treated as an asymptotic series and cut almost anywhere after the contribution of successive levels has become negligible. As the temperature is raised, however, the breadth of this minimum narrows until ultimately there is no level at which the contributions of successive levels become small. As soon as this happens, the advantage of an obvious cut-off point is lost and, in fact, the partition function begins to depend strongly on the choice of cut-off. This is obviously a signal that the theory on which the calculation is based has become inadequate, and this is indeed the case. Care must be taken even when this problem does not appear to exist. Exact partition function expressions are often approximated by series which are cut-off in a manner appropriate for low temperatures. When these series are extended to high temperatures, they sometimes give convergent, albeit wrong, results due to the neglect of terms not needed at low temperatures but needed at higher temperatures.^{16d} These neglected terms contain the divergence problem.

An interesting way of handling these divergences has been devised by Woolley¹⁷ and studied in some detail by several others.¹⁸ In this approach, sometimes referred to as physical cluster theory, no distinction is made between a molecule whose constituent atoms are bound together by means of covalent bonds and a physical cluster of these atoms for separations and conditions for which the weaker van der Waals interactions are appropriate. Reflection indeed leads one to the conclusion that any distinction which might be made between these would indeed be artificial.

The divergence which arises from the summing of the energy levels of atoms and atomic ions over highly excited states of the outer electron has been considered in a number of different ways in the literature. Clearly, the representation of the partition function of the atom in the mixture as a sum over energy levels of the isolated atom is an approximation to the actual many body problem. At ordinary temperatures, this approximation is reasonable since the number of atoms in any but the lowest lying energy levels is quite small. Using semi-classical arguments, it is easy to see that the Bohr radii for such levels are quite small and that, therefore, the "paths" of the outer electrons of different atoms do not overlap. As the temperature is raised, the situation changes and the Bohr orbits become sufficiently large for there to be overlap even at ordinary densities. The problem has therefore become a many body problem whose partition function can no longer be approximated by a product of one particle functions.

Several workers^{19,20,21} have devised density dependent cut-off methods which are essentially variations of an approach due to Urey^{22a}, Fermi^{22b} and also contained in some unpublished work of Bethe^{22c}. In these approaches, the energy levels are summed only through those quantum numbers for which the Bohr radius is less than some function of the average interparticle distance. The problem now becomes density and temperature dependent, the density determining

the average interparticle distance and the temperature the Bohr radius of the outer electrons as well as the probability of there being close collisions.

There are thus two main approaches to the problem of calculating the ideal gas partition functions of atoms and atomic ions depending on the temperature range of interest and the ionization energy. Up to moderately high temperatures, the sums can be cut-off at a relatively low lying level based on the smallness of successive contributions. At high temperatures, a cut-off can be taken which depends on temperature and density and which may vary for a given atomic species from mixture to mixture.

Since the quantum number takes on discrete values, it is possible for the summation to take on discontinuities as a function of temperature and density²¹. These discontinuities occur where a change occurs in the final quantum number accepted under the cut-off criterion. A way to reduce this problem has been proposed by Woolley¹⁷ (and independently by Gilmore²⁴). In these approaches, the partition function is divided into a sum of two parts. One of these is the contribution due to states below some quantum number n_A which is always less than n_c , the density dependent cut-off. The other is^A due to the contribution of the levels between n_A and n_c considered now to be the levels of one electron on an ionized atom. The levels between n_A and n_c are, in fact, considered to be hydrogen-like on the ionic core. This method^C has the advantage of allowing one to use tables of ideal gas partition functions and a cut-off criterion which depends on the species only through the nuclear charge. It is, therefore, of considerable computational advantage. Woolley's method is designed particularly for treating the ionized gas as an ionic solution within the theoretical framework set up by Mayer^{23a} and Poirier.^{23b}

It should be clear from the preceding discussion that there are several ways in which one can approach the divergence problems which arise in the sum over states associated with the calculation of the ideal gas partition functions of the individual species in a chemical reacting mixture. It is imperative, no matter which of these methods is used, that the counting of states for a given species above the dissociation or ionization limit for its constituents be done in a manner which is consistent with the counting of the states for these constituents themselves. If this is not done properly, a portion of the phase space for the mixture will have been included at least twice in the statistical mechanical development for the mixture thermodynamic properties. Thus, one might mistakenly include the states associated with the separated atoms as a molecular state with a van der Waals intermolecular potential and include the same states as free atoms with a correction for nonideality. A consistent way in which this problem can be avoided has been described by Haar.^{18c}

6. THE THERMODYNAMIC PROPERTIES OF THE MIXTURE

Once the thermodynamic functions for the individual species have been calculated at the temperature of interest and once the energies $\Delta E_0^0/RT$ have been chosen, it is possible, in principle, to solve for the species concentrations using either the method of free energy minimization (minimization of (6) subject to (7)) or the equilibrium constant method (solution of (19) subject to (18))

and to determine the concentrations of all species at that temperature as a function of the most useful thermodynamic variable (e.g. pressure, density, etc.). Given these concentrations and the properties for the individual species, one can then calculate the thermodynamic properties of the ideal gas mixture. In this section, we shall indicate how this can be done. Real gas corrections to these expressions are included below in an appendix.

According to our definitions of concentration and compressibility factor, the compressibility factor for the ideal gas relative to that at standard conditions is simply a sum over species concentrations, the sum going over both the derived and reference species. Thus,

$$Z = \frac{PV}{RT} = \sum_{i=1}^{\ell} C_i \quad (23a)$$

where, as stated earlier, C_i is the number of moles of species i relative to one mole in a reference state and Z is the compressibility factor, defined to include the number of moles, also with respect to a reference state. As stated earlier, the choice of the reference state is a matter of convenience in scaling these quantities.

The internal energy can be calculated from

$$\frac{E}{RT} = \sum_{i=1}^{\ell} C_i \frac{E_i}{RT} \quad (23b)$$

where $E_i = (E_T^O - E_O^O)_i + (E_O^O)_i$ and

where $(E_T^O - E_O^O)_i$ is calculated from statistical mechanics.

The entropy is given by

$$\frac{S}{R} = Z \left[\sum_{i=1}^{\ell} x_i \left(\frac{S^O}{R} \right)_i - \sum_{i=1}^{\ell} x_i \ln x_i - \ln \left(\frac{P}{P^O} \right) \right] \quad (23c)$$

where P^O is the pressure of the thermodynamic standard state. All other thermodynamic potentials can be written in terms of combinations of (23a,b,c).

Among the gas properties of interest are the derivatives of the thermodynamic potentials. These lead to such properties as the specific heat and sound velocity. Such properties are often obtained by numerical differentiation of tables of the thermodynamic potentials.²⁵ The best of such methods requires considerable caution in its application. It is necessary to be careful in handling the end points and care must be taken to ensure that the data points are neither too close together nor too far apart. Numerical differentiation is entirely unnecessary, however, since the derivatives can be obtained as the solutions of sets of c linear equations in c unknowns, c being the number of reference species in the mixture^{26,27}. Several authors^{28,29} have developed similar approaches in which, however, the derivatives are expressed in terms of the solutions of l linear equations in l unknowns, l being the total number of species in the mixture. The difference between c and l is generally quite large. For high temperature air, for example, $l = 30$ while $c = 6$. It should be understood, however, that the reduction from l equations to c equations occurs only under ideal gas conditions (i.e. $\gamma_i = 1$). When real gas effects are included, it is always necessary to solve a set of l equations in l unknowns for the derivatives. We shall proceed to derive the linear equations for the derivatives within the framework of the equilibrium constant method. The results obtained are, of course, valid in either approach.

The derivatives required can in all cases be written in terms of the derivatives of properties which are additive functions of the properties of the individual constituents. This means that it is only necessary to calculate the derivatives of functions of the form

$$Y = \sum_{i=1}^l C_i Y_i^0 \quad (24)$$

where Y_i^0 is an arbitrary ideal gas property for the i^{th} constituent.

Thus, for the specific heat at constant volume one has

$$\frac{C_v}{R} = \left(\frac{\partial E}{\partial T} \right)_p \quad \text{where } E = \sum_{i=1}^l C_i E_i$$

The difference in the specific heats is given by

$$\frac{C_p - C_v}{R} = \frac{1 + \frac{T}{Z} \left(\frac{\partial Z}{\partial T} \right)_\rho}{1 + \frac{\rho}{Z} \left(\frac{\partial Z}{\partial \rho} \right)_T} \quad \text{where } Z = \sum_{i=1}^l C_i$$

and the ratio of specific heats is then obtainable from $\gamma = C_p/C_v$. The sound velocity can be written

$$\frac{a}{a_0} = \gamma R T Z \left[1 + \frac{\rho}{Z} \left(\frac{\partial Z}{\partial \rho} \right)_T \right]$$

Useful in aerodynamic calculations²⁹ are the following

$$\gamma_{P,\rho} = \left(\frac{\partial \ln P}{\partial \rho} \right)_S = \gamma \left[1 + \frac{\rho}{Z} \left(\frac{\partial Z}{\partial \rho} \right)_T \right]$$

$$\gamma_{T,\rho} = \left(\frac{\partial \ln T}{\partial \ln \rho} \right)_S = 1 + \frac{1 + \frac{T}{Z} \left(\frac{\partial Z}{\partial T} \right)_\rho}{C_v/R} Z$$

$$\text{and } \gamma_{T,P} = \frac{1}{1 - \left(\frac{\partial \ln T}{\partial \ln P} \right)_S} = \gamma \left[1 + \frac{T \left(\frac{\partial Z}{\partial T} \right)_\rho \left(1 + \frac{T}{Z} \left(\frac{\partial Z}{\partial T} \right)_\rho \right)}{\left[1 + \frac{\rho}{Z} \left(\frac{\partial Z}{\partial \rho} \right)_T \right] C_v/R} \right]^{-1}$$

The above expressions contain derivatives of additive functions as in (24) which are either with respect to temperature at constant density or are with respect to density at constant temperature.

Let us first consider the derivatives at constant density, i.e., we

shall consider the evaluation of the quantity $(\frac{\partial Y}{\partial T})_p$. Now, from (24)

$$(\frac{\partial Y}{\partial T})_p = \sum_{i=1}^l (\frac{\partial C_i}{\partial T})_p Y_i^o + \sum_{i=1}^l C_i (\frac{\partial Y_i^o}{\partial T})_p \quad (25)$$

The second term contains the species ideal gas function $(\frac{\partial Y_i^o}{\partial T})_p$ which can be computed directly from the partition function of the i th species. The C_i are obtained as solutions of the equilibrium equations. The second term is therefore simply a cumulative sum involving known quantities. Since the Y_i^o which appear in the first term are also known, the problem of evaluating (25) reduces to the determination of the concentration derivatives. We shall do this for the ideal gas (i.e., $\gamma_i = 1$) only, the extension to conditions where this is not appropriate (i.e., $\gamma_i \neq 1$) being left to the interested reader. Taking the derivative of (19) yields

$$(\frac{\partial \ln C_i}{\partial T})_p = (\frac{\partial \ln \bar{K}_i}{\partial T})_p + \sum_{j=1}^c v_{ij} (\frac{\partial \ln C_j}{\partial T})_p \quad (26)$$

where j runs over the reference species only. There are also the conservation equations (20),

$$X_j = \sum_{i=1}^l v_{ij} C_i = \sum_{i=1}^{l-c} v_{ij} C_i + \sum_{i=l-c+1}^l v_{ij} C_i \quad j = 1, \dots, c$$

Since $v_{ij} = \delta_{ij}$, the Kronecker delta for reference species, this can be written

$$X_j = \sum_{i=1}^l v_{ij} C_i + C_j \quad j = 1, \dots, c \quad (27)$$

where, again, j runs over the reference species only. Differentiating (27) and using (26), there results

$$B_j = - \sum_{k=1}^c A_{jk} \left(\frac{\partial \ln C_k}{\partial T} \right)_\rho \quad j = 1, \dots, c \quad (28)$$

where

$$B_j = - \sum_{i=1}^l v_{ij} C_i \left(\frac{\partial \ln \bar{K}_1}{\partial T} \right)_\rho$$

and

$$A_{jk} = \sum_{i=1}^l v_{ij} v_{ik} C_i + \delta_{kj} C_k \quad (29)$$

and where

$$\left(\frac{\partial \ln \bar{K}_1}{\partial T} \right)_\rho = \frac{1}{T} \left[\frac{E_1}{RT} - \sum_{j=1}^c v_{1j} \frac{E_j}{RT} \right]$$

is a known quantity, with E_i the internal energy of the i^{th} species. The c unknowns, $\left(\frac{\partial \ln C_k}{\partial T} \right)_\rho$, i.e. the derivatives of the reference species, constitute the unknown vector in (28). Having solved these equations, e.g., by inverting the matrix A , (26) can be used to calculate the derivatives of the ordinary species.

Let us now consider derivatives with respect to the density at constant temperatures, i.e. $\left(\frac{\partial Y}{\partial \rho} \right)_T$. Differentiation of (19) leads to the relations

$$\left(\frac{\partial \ln C_i}{\partial \rho} \right)_T = + \frac{w_i}{\rho} + \sum_{j=1}^c v_{ij} \left(\frac{\partial \ln C_j}{\partial \rho} \right)_T \quad (30)$$

On the other hand, differentiation of (27) yields

$$0 = \sum_{i=1}^l v_{ij} C_i \left(\frac{\partial \ln C_i}{\partial \rho} \right)_T + C_j \left(\frac{\partial \ln C_j}{\partial \rho} \right)_T$$

Combining the latter with (30) leads to

$$B_j = - \sum_{k=1}^c A_{jk} \left(\frac{\partial \ln C_k}{\partial p} \right)_T \quad j = 1, \dots, c \quad (31)$$

where

$$B_j = \sum_{i=1}^l \frac{v_{ij} C_i \omega_i}{\rho}$$

and where A_{jk} is again given by (29). Since the coefficient matrix A_{jk} is identical in both cases, one can use essentially the same computer program to solve (28) and (31). These solutions are then substituted into (26) and (30) to obtain the derivatives of the remaining species.

It should be noted that equations (28) and (31) are each c linear equations in the derivatives of the c reference species. At this point it should be clear that, fundamentally, the equilibrium constant approach to the problem is one of solving c non-linear equations in c unknowns.

As mentioned above, the ability to express the derivatives in terms of c equations in c unknowns is peculiar to the ideal gas approximation. As soon as concentration dependent terms are introduced in the activity coefficients, concentrations of derived species appear on the right hand side of (19) and hence on the right hand sides of (26) and (30). This, then, requires the solution of linear equation in unknowns for the evaluation of the concentration derivatives. It may still be possible, however, to use these ideal gas expressions for the derivatives under conditions where the concentrations include real gas effects. This can be done when $\gamma_i \neq 1$.

but $\left(\frac{\partial \gamma_i}{\partial p} \right)_T$ and $\left(\frac{\partial \gamma_i}{\partial T} \right)_p$ are negligible for major constituents. This can even

be extended to situations in which these derivatives are small but not negligible by developing additive expressions for corrections due to the contribution of these derivatives of the γ_i . These expressions could then be evaluated by an approximate numerical scheme.

7. NUMERICAL METHODS

A. INTRODUCTION

We now turn to the central problem of this report, namely that of

solving for the species concentrations. This can be done within the framework of either the free energy minimization method or the equilibrium constant method.³⁰ These are, of course, entirely equivalent methods³¹ and the decision to choose one over the other is mainly a matter of taste. For the purposes of this report, numerical methods will mean those methods appropriate to digital calculators. It is interesting to note that chemical equilibrium equations have been solved using analog computers.³² Such methods are considered to be outside the province of this report, however.

Within the framework of the two methods the literature can be further divided between numerical approaches which are specifically tailored to a particular chemical problem and those which are general purpose approaches. Special purpose approaches mainly predate the advent of high speed electronic computers. At that time the carrying out of involved algebraic operations was much to be preferred over long and tedious numerical calculations which had to be done on a slide rule or desk calculator. These special purpose approaches, in the main, consist of the reduction of the c equations (21) to one or two equations by successive substitution. With the increasing availability of large scale high speed computers whose main purpose is just the carrying out of tedious repetitious numerical operations, the need for the development of such special purpose schemes has disappeared.

Intermediate between these special purpose schemes and general purpose methods are a number of approaches³³ which apply to systems for which the concentrations of those derived species which contain more than one reference species is small. These approaches are based on the fact that the neglect of such species serves to uncouple equations (20) thereby converting the problem into that of solving a set of c independent non-linear equations. Such approaches, where they are appropriate, can be useful in preliminary studies of chemical systems.

It is interesting to note that, from a numerical point of view, both the free energy minimization and the equilibrium constant methods, require the determination of a set of values of the concentrations of the reference species which minimizes some function of these concentrations. This is obvious for the free energy minimization method for which the free energy itself is being minimized. In the equilibrium constant method, on the other hand, the exact solution of a set of equations is required. From a numerical point of view, this can also be cast into a form requiring a minimization, namely the minimization of an error function which represents departures from the solution.³⁴ Thus, the solution of an arbitrary set of equations

$$\psi_i(x_1, \dots, x_n) = 0 \quad i = 1, \dots, n \quad (32)$$

is equivalent to the minimization of the function

$$\phi = \sum_{i=1}^n |\psi_i|^2 \quad (33)$$

with respect to the parameters x_i ($i = 1, \dots, n$). This replacement by a minimization problem is not unique, however. In particular, if α_{ij} are the elements of any positive definite matrix α , then the solution of the set of equations (32) is also equivalent to the minimization of the function $\phi = \sum_{ij} \psi_i \alpha_{ij} \psi_j$ with both minima being identical. (33) is thus seen to be the special case where $\alpha = I$ the unit matrix. Since both methods lead to a numerical minimization problem, it is possible to describe the solution of the equations appropriate to either in the same numerical mathematical language.

Non-linear problems generally cannot be solved in closed form. In the present case, the fact that the problem is non-linear can perhaps best be seen in equations (21) of the equilibrium constant method where the unknowns, C_j , appear as products raised to powers (some of which are negative). Non-linear equations of this kind will certainly not be soluble in closed form, particularly in such a way as to be capable of handling different chemical systems. It should be noted in this regard, that each chemical system requires the use of a different T matrix and hence a different set of exponents v_{ij} in (21). This, in turn, requires the solution of a different set of non-linear equations. In the absence of a general closed form method of solution, therefore, it is necessary to develop a purely numerical approach to the solution of the problem of minimizing ϕ in (33).

Such methods start with a guess at the set of variables x_1, \dots, x_n in (32). This guess is substituted into ϕ in (33) and generally found not to be the set of variables which minimizes ϕ . Procedures are then invoked to improve on the guess in a systematic way. If the improvement procedure is properly designed, that set of values of the variable x_1, \dots, x_n is ultimately determined which does in fact minimize the function ϕ within a preassigned tolerance.

Clearly, whether use is made of the free energy minimization method or the equilibrium constant method, and, in fact, regardless of whatever numerical method is chosen, there must ultimately result a minimum value of ϕ . Since the function ϕ describes a surface in the n -dimensional space whose coordinate axes are the concentrations of the reference species, all numerical methods which can be devised for finding the minimum of ϕ must be geometrically equivalent to starting from some initial point on this ϕ surface and searching for the surface minimum. For this reason all such methods are referred to as search methods. The function being minimized (i.e. ϕ in (33)) is referred to as the objective function.

Non-linear problems which are fundamentally different from each other make use of different objective functions. As will be seen below, it can also be true that different numerical approaches to the same non-linear

problem can be based on the use of different objective functions. In the latter case, it should be obvious that the n-dimensional surfaces corresponding to the different objective functions should have the same coordinates (but not necessarily the same value) for the objective function at their respective minima. This can usually be shown to be trivially true since these objective functions most often differ from each other by functions which vanish at the location of the minimum. Even when this is not so, they, of necessity, differ by functions whose surfaces also have minima at this same location.

There are a number of objective functions which have been widely used in the numerical methods associated with the direct free energy minimization and equilibrium constant methods. Consider the direct free energy minimization method. Here, the objective function can simply be taken to be the free energy of the mixture. In another numerical approach to this method,³⁵ constants times the sum of the squares of the left-hand sides of (7) are added to the free energy and the total function taken as the objective function. Since the left-hand sides of (7) vanish at the solution, this addition to the free energy has no effect on the solution. In fact, since these added quantities are positive away from the solution, they tend to increase the magnitude of the objective function away from the solution over the value it would have if it were simply the free energy. As a result, they tend to magnify the depth of the minimum in the objective function over that obtained using the free energy minimum alone. Although other objective functions are possible, they will not be included in this discussion.

While the equilibrium constant method can likewise be stated in more than one way according to the choice of objective function,³⁶ we shall restrict ourselves to that based directly on satisfying the relevant equations. Thus, the set of equations (21) will be satisfied if and only if the proper values are used for the reference species. In the spirit of equation (33) it is possible to define a set of functions of the concentrations of the reference species

$$\psi_1(C_1, \dots, C_c) = \sum_{i=1}^k v_{ij} \bar{K}_1 (\sigma/\rho_o)^{\omega_i} \prod_j (C_j^{v_{ij}})^{-x_j}$$

The problem of solving (21) is then equivalent to the minimization of the objective function

$$\phi = \sum_{i=1}^c |\psi_i|^2$$

It should be noted that the addition of the Gibbs free energy to this ϕ results in yet another possible objective function and, in fact, is essentially one of the objective functions described for the direct free energy

minimization method.

It should be obvious that the same search method can, in principle, be used for all minimization problems. For this reason part of what follows contains descriptions of and references to general search methods (i.e. not specific to the chemical equilibrium problem). In practice, however, it is often found that search methods need to be empirically tailored to the particular non-linear problem at hand. This is not to say, in the problem under discussion, that the search methods must necessarily be tailored to the particular chemical system of interest. Rather, these methods must be adjusted to handle the chemical equilibrium problem in a manner different from an adjustment made for some other non-linear problem. This says, in essence, that variations of conditions within the same non-linear problem (e.g. the variation due to changing the chemical system in the equilibrium problem) will result in objective function surfaces which are much more nearly alike than are the surfaces associated with objective functions for quite different non-linear problems.

Each chemical problem might be expected to have an optimum numerical method of solution. The chances of there being such an optimum numerical method of solution for the wide range of chemical problems associated with all possible variations in the T matrix is quite small, however. We shall, in fact, assume that no such general optimum method exists and shall aim at the description of general search methods which should have a high probability of converging to the correct answer for almost all chemical systems. It should be pointed out, however, that there can also be considerable advantage to making small adjustments on the search method for each particular chemical system where such adjustments are feasible. A particular method with which the author has considerable experience and which has been found to converge rapidly in a manner which is independent of the initial guesses will be discussed below in some detail.

A general philosophical point relating to search methods needs to be emphasized. That is, there are no restrictions on the procedures which can be devised for going from point to point on the ϕ surface, provided only that a proper test is used for the determination of when the surface minimum is reached. In particular, the precise method for the development of the path to the minimum need have no relationship to the chemistry of the problem and, for that matter, none to its mathematics. In fact, it is not even necessary to follow a point having a particular value of ϕ by one with a smaller value of ϕ , if this turns out to be convenient. As might be expected, however, search methods have been developed in which a sequence of points is traced out on the surface in such a way that the ϕ associated with a given point is indeed guaranteed to be less than the ϕ associated with the preceding point. The ability to do this guarantees convergence to the answer in the sense that successively decreasing ϕ ultimately leads to its minimum value. This guarantee is sometimes obtained at the cost of slow convergence, however.

The starting point has no more a priori physical significance than a point used in any other iteration. It follows, therefore, that the

particular method chosen for determining initial guesses need have no relation to the chemistry or mathematics of the problem just as for other iteration points. Many of the methods as described in the literature require starting from points which satisfy the mass balance equations (20). Such a restriction is entirely unnecessary, however, since a proper test for the solution will automatically guarantee that the equations (20) are satisfied at the accepted solution. In what follows, we shall have little to say about methods for choosing starting values.

While it is generally not possible rigorously to prove convergence for a search method except in the vicinity of the minimum, empirically it is found that most search methods do converge even from points quite far removed from the solution. The ease with which this can be done for a particular method, or equivalently, the sensitivity of the method to the choice of a starting point, depends very strongly on the method itself.

It should be clear from the preceding discussion that central to the solution of non-linear minimization problems is the proper choice of a criterion by means of which one determines that the solution has been found. Criteria for solutions which are appropriate to the problems of interest here are obvious. Despite this, they are not always used. Clearly, every surface minimum, regardless of the problem, is characterized by the requirement that the derivatives of the objective function with respect to the unknown variables are each less than some arbitrarily small value. This criterion would appear to be a natural one for the direct free energy minimization method. In the case of the equilibrium constant method, there is the further requirement that the equations (19) and (20) themselves must be simultaneously satisfied, (or equivalently, that ϕ in (33) is sufficiently small). An intermediate method can also be developed by using the direct free energy minimization method of solution but requiring that (13) be satisfied at the solution, the μ_1 being given by (8).³⁵ Despite these rather obvious criteria, however, search methods all too often use as a criterion for solution the condition that changes in all the unknowns from one iteration to the next become vanishingly small at the minimum.³⁷ Although the latter condition generally yields the same results as the former, it is not guaranteed to do so.

B. SEARCH METHODS

In recent years, an entire literature has developed which deals with non-linear search methods.³⁸ This literature consists mainly of descriptions of various methods with occasional reports of experience with particular problems. There is very little in the way of general proofs either for optimization procedures or for convergence except, perhaps, for points near the solution where linearization is valid. We shall only describe the general characteristics of non-linear search methods leaving the reader the option of going to the literature for more detailed reviews or for the details of specific methods.

The decision to choose one particular search method over all others will

generally depend, at least in part, on such non-mathematical criteria as relative speed of attaining the solution and ease of programming. It will also depend on how often a particular problem is to be solved and for how many different chemical systems. As computing machines become faster, the need for a simply programmable method tends to outweigh considerations of machine speed. On the other hand, the availability of generalized subprograms for the complicated mathematical and logical details of a method tends to reduce the programming time required.³⁹ It is clear from this, that criteria for the choice of one search method over another depend to a large extent, on the details of the computing facility available for the solution of the problem. In the following, we shall describe a number of different search methods in general terms and shall include alternatives which might serve to reduce computing time. The coverage of these methods is not meant to be exhaustive. More complete discussions will be found in the several review articles included among the references which deal with non-linear search methods.

The problem of finding the minimum of a multidimensional surface is a special case within the general class of problems of finding extreme values. Any method developed for the express purpose of finding minima of surfaces can be applied, with at most minor modifications, to the problem of finding surface maxima and vice versa. The latter are more natural within the framework of the disciplines of economics and operations research. This correspondence was specifically taken advantage of in an approach developed at the Rand Corporation in which the equations appropriate to the method of the direct minimization of the free energy were solved by means of linear programming techniques originally developed for the solution of operations research problems. This approach is discussed quite lucidly in a series of Rand reports and will not be considered here.

A non-linear problem in a set of unknowns can always be converted to a linear problem in a set of deviations from the current values of the unknowns. In order to do this rigorously, it is necessary to make the assumption that such deviations are negligible compared to the current values. This can be done in (19) near $C_j^{(k)}$, the k^{th} iterate for the reference species. By taking $C_j^{(k+1)} = C_j^{(k)} + \delta C_j$ and neglecting products of the δC_j , there results a set of linear equations for the δC_j . These can be solved for the δC_j and a new guess $C_j^{(k+1)}$ obtained. This method is rigorous very near the solution point. For points far from the solution, however, there is not even the guarantee that the corrections δC_j will be in the proper direction. In spite of this the method has been used successfully.⁴⁰

Another method for linearizing non-linear problems is to take a Taylor expansion about the current values of the unknowns and neglect terms involving products and squares of deviations. This method differs from the simple expansion in that the first derivatives at the current guess point appear in the linear equations. This latter method of linearization is essentially the Newton-Raphson method for the solution of sets of non-linear equations. We shall indicate several ways in which this method has been applied to the

chemical equilibrium problem. A common variation of this approach makes use of a Taylor expansion of the first derivatives about the minimum. In this approach, the linear terms in the deviations contain the second derivatives of the objective function.⁴⁰ The latter approach is often referred to as the Gauss-Newton method.

Search methods for the development of paths along the surface to the minimum can also be referred to as iterative methods. This general class of numerical methods, starts with a guess value, which is substituted into the equations to be solved. On the basis of the result of this substitution, a new value is determined which then becomes the guess value for a repeat of this procedure. This process is continued until, given a convergent method, a solution is obtained. Iterative methods can be written in terms of a function of the variables which gives a prescription for calculating the next guess from a given guess point. In particular, this function defines a sequence of operations

$$\vec{x}^{(k+1)} = \Gamma(\vec{x}^{(k)}) \quad (34)$$

The functions Γ can be viewed as operators which, when operating on a guess value \vec{x}_k , produce the next guess value \vec{x}_{k+1} . This operation can also be given a geometrical interpretation by writing the sequence

$$\vec{x}^{(k+1)} = \vec{x}^{(k)} + \lambda \vec{\mu}^{(k)} \quad (35)$$

where $\vec{\mu}^{(k)}$ is a unit vector in the direction of the next guess with λ the magnitude of the step in that direction. (35) is generally used to describe descent methods, $\vec{\mu}$ then always being taken as a vector in the general direction of the minimum.

Iteration methods are generally described as being either of the Newton-Raphson type or of the descent type, although the distinction is not always clear.³ In the Newton-Raphson approach, $\Gamma(\vec{x})$ is obtained from a truncated Taylor series about the solution. For example, suppose that the surface minimum occurs at the point $\vec{x}^{(0)}$ with $\vec{x}^{(1)}$ a point close by. It follows, then, that $\psi(\vec{x}^{(0)}) = \psi(\vec{x}^{(1)}) + J(\vec{x}^{(1)}) (\vec{x}^{(0)} - \vec{x}^{(1)})$ where $J(\vec{x})$ is the matrix of the partial derivatives of $\psi(\vec{x})$, i.e. $J_{ij} = \frac{\partial \psi}{\partial x_j}(\vec{x})$. If $\vec{x}^{(0)}$ is at the minimum, it follows that $\psi(\vec{x}^{(0)}) = 0$ so that, solving for $\vec{x}^{(0)}$, there results

$$\vec{x}^{(0)} = \vec{x}^{(1)} - J^{-1}(\vec{x}^{(1)}) \psi(\vec{x}^{(1)})$$

If in a sequence of iterations the k^{th} point is sufficiently near the minimum, it follows that the solution can be obtained as the $(k+1)^{\text{th}}$ point by solving the equation

$$\vec{x}^{(k+1)} = \vec{x}^{(k)} - J^{-1}(\vec{x}^{(k)}) \psi(\vec{x}^{(k)}) \quad (36)$$

While this is only rigorously correct at the solution, it is used in the Newton-Raphson approach at all points on the surface as a means of determining a sequence of points $\vec{x}^{(k+1)}$, $\vec{x}^{(k+2)}$, ..., etc. which define a path to the minimum. It should be noted that, for the Newton-Raphson method the Γ operator is given by

$$\Gamma(\vec{x}) = \vec{x} - J^{-1}(\vec{x}) \psi(\vec{x}) \quad (37)$$

Substitution of (37) into (34) and comparison with (35) shows that there is a descent version of the Newton-Raphson search method with the direction vector given by

$$\lambda \vec{u} = -J^{-1}(\vec{x}) \psi(\vec{x})$$

At the solution, (37) becomes $\Gamma(\vec{x}^{(k+1)}) = \vec{x}^{(k+1)}$ so that $\vec{x}^{(k+2)} = \vec{x}^{(k+1)}$ and the differences between successive iterations eventually vanish. As has been mentioned, this can be used as a basis for a criterion for solution. Thus, a solution is said to have been reached when the change between successive values of all components of the vector \vec{x} become less than some fraction of their current values. Unfortunately, this is not a necessary and sufficient condition for a solution. Thus, while we have shown this property to hold at the solution, (necessary condition), it is possible that for a particular search method a point on the surface can satisfy this condition away from the solution. Thus, satisfying this criterion does not guarantee a solution (sufficient condition).

Mention has been made of a version of the Newton-Raphson method (often referred to as the Gauss-Newton method) which makes use of second derivatives.⁴¹ This can be written in vector notation in a form similar to (36). For $\vec{x}^{(k+1)} - \vec{x}^{(k)}$ small, the matrix of first derivatives, $J(\vec{x})$ can be expanded about the point $\vec{x}^{(k)}$ to terms linear in the difference $\vec{x}^{(k+1)} - \vec{x}^{(k)}$. This results

$$= J(\vec{x}^{(k)}) + H(\vec{x}^{(k)}) \cdot (\vec{x}^{(k+1)} - \vec{x}^{(k)})$$

where $H(\vec{x})$ is the matrix of second derivatives generally referred to as the Hessian matrix. If the assumption is made that $\vec{x}^{(k+1)}$ is the solution point, it follows that $J(\vec{x}^{(k+1)}) = 0$ and the above relation becomes

$$0 = J(\vec{x}^{(k)}) + H(\vec{x}^{(k)}) \cdot (\vec{x}^{(k+1)} - \vec{x}^{(k)})$$

or:

$$H(\vec{x}^{(k)}) \cdot \vec{x}^{(k+1)} = H(\vec{x}^{(k+1)}) \cdot \vec{x}^{(k)} - J(\vec{x}^{(k)})$$

from which

$$\vec{x}^{(k+1)} = \vec{x}^{(k)} - H^{-1}(\vec{x}^{(k)}) J(\vec{x}^{(k)})$$

quite analogous to (36). In this case $\Gamma(\vec{x})$ is given by

$$\Gamma(\vec{x}) = \vec{x} - H^{-1}(\vec{x}) J(\vec{x})$$

In what follows we shall discuss the Newton-Raphson method only in the form (36).

Many variations of the Newton-Raphson search algorithm (i.e. (36)) have been devised through variation of the definition of $J(\vec{x})$. These alternate methods are mainly used when the calculation of $J(\vec{x})$ and its inverse either involves excessive computing time or is overly complex. The simplest variation involves a simple iteration. In that case $J(\vec{x}) = \lambda I$, with I the unit matrix, and the algorithm for the choice of successive values

$$\Gamma(\vec{x}) = \vec{x} - (\vec{x}) \lambda \psi(\vec{x})$$

which, at the solution becomes $\Gamma(\vec{x}_{k+1}) = \vec{x}_k$. As will be seen below this approach falls within a category of methods which we have designated direct search methods. An appropriate value of λ can be found empirically generally through monitoring the behavior of the \vec{x} vector in successive iterations. The value of λ used will depend strongly on the nature of the function $\psi(\vec{x})$. For example, consider the one-dimensional problem $\psi(\vec{x}) = 0$. If $\psi(\vec{x})$ is such that $x^{(1)} < x^{(0)}$ implies $\psi(\vec{x}) > 0$ then clearly $\lambda > 0$ is required. If, on the other hand, $x^{(1)} > x^{(0)}$ implies $\psi(\vec{x}) < 0$, $\lambda < 0$ is required. These requirements would easily be obtained empirically.

A more complicated variation of the Newton-Raphson method involves replacing the "tangent" matrix $J(\vec{x})$ by a "secant" matrix $J(\vec{x})$.⁴² In this approach, the partial derivatives in the J matrix are replaced by finite differences based on neighboring solution points. For an n dimensional ϕ space (i.e. for n unknowns), the secant approximation requires having in hand $n + 1$ neighboring values. The method thus does not really get under way until the objective function has been evaluated at $n + 1$ points. The procedure can be started by choosing, somewhat arbitrarily, these $n + 1$ points, evaluating the function, calculating the elements of the matrix J and proceeding to invert J as in the Newton-Raphson method. Since the derivatives of the function do not have to be evaluated, computing time is reduced. Since the secants make use of stored evaluations of the objective function at the $n + 1$ points, the programming is also simplified. Since the method still requires a matrix inversion for determining $J^{-1}(\vec{x})$ from $J(\vec{x})$, the saving in machine time will be modest. A dramatic reduction in computational time can be had by means of a variation on the secant version of the Newton-Raphson method in which each component x_j of the unknown vector \vec{x} is treated separately thus eliminating the need for matrix inversion. That approach is associated with the name of Wegstein⁴⁴ and will be described below among the direct search methods.

An interesting variation of the Newton-Raphson method has recently been described.⁴¹ In that approach, the coordinate system in parameter space is rotated into the space spanned by the eigenvectors of J . In that space, J can be written in diagonal form. The advantage of this approach is that since the new "parameters" (i.e., the eigenvectors of J) are orthogonal, they do not interact with each other so that the minimization can be carried out independently for each.

A number of methods have been developed for the solution of chemical equilibrium problems which make use of a Newton-Raphson search method. The two most widely used are one due to Brinkley² and a second due to Huff et al.⁴ The relationship between them is discussed in some detail in the review of Zelesnik and Gordon.⁴ Each method is sufficiently well described in the literature to preclude the need for a description here. Brinkley's approach is, of course, built around the solution of a set of equations whose number is the same as the number of reference species. It is interesting to note that the method of Huff et al, as originally described, considers both the reference species and the derived species on an equal footing thus requiring the solution of ℓ equation for the ℓ composition variables. Since ℓ can become prohibitively large for matrix techniques, methods for reducing this requirement are of interest. Zelesnik and Gordon indicate that, as expected, the method can be converted to one in which only the reference species are required, thereby reducing the problem to that of solving c equations in c unknowns, where $c < \ell$ is always the case. They indicate, however, that this can result in convergence problems unless the reference species are carefully chosen so as to be major constituents or, if not, unless the initial guesses are good. This problem does not appear to arise when all ℓ equations are solved presumably since these always contain the major constituents.

C. DIRECT SEARCH METHODS

Search methods fall into two categories on the basis of the ease with which they can be applied to new problems. This can be of considerable practical importance in the chemical equilibrium problem. For example, after programming an ideal gas calculation, one might wish to add in real gas effects by relaxing the restriction $\gamma_i = 1$. For some search methods this can pose a major reprogramming problem, while for others, the conversion is rather simple. These two classes of search methods can be described, roughly, in terms of the extent to which they depend on the content of the equilibrium equations.

Search methods of the general Newton-Raphson type require considerable detail since they call for the calculation of first (and sometimes second) derivatives of the objective function in addition to the evaluation of the objective function itself. Reprogramming for such methods can call for considerable effort. On the other hand, search methods exist which at each step require only that the objective function be evaluated. Such methods we shall designate direct search methods since, in the case of the most obvious one, the minimum in the objective function surface is sought by a direct search in variable space. The usual definition of direct search methods is much more narrow than this. We shall, in fact, include among our direct search methods certain ones that are variations of approaches not normally defined as being of the direct search type, e.g. variations of the Newton-Raphson method. This underlines the arbitrariness of these classifications.

There are several advantages to be had from the use of direct search methods. Since only the objective function is evaluated, a minimum of reprogramming effort is required when the objective function is altered. Furthermore, the simplicity of the search aspect allows for simple initial programming thereby reducing the time required for going from the development of the problem to the working computer program. Experience has also shown that direct search methods can be successful for problems which are poorly conditioned for the other methods.^{43,44} An example might be a problem for which the matrix of the derivatives of the objective function with respect to the unknowns is ill-conditioned in some part of variable space even far removed from the solution. Since that matrix plays a key role in the Newton-Raphson method, there can be trouble with it if an interaction happens to come near such regions of ill-conditioning.

Perhaps the simplest of the direct search methods is one that merely involves testing the objective function in a stepwise variation of the unknown parameters (perhaps on a grid), accepting only those changes which reduce that function. The pattern search method of Hooke and Jeeves⁴³ is an improvement over this simplistic approach. Their approach makes use of information obtained but usually ignored in a simple step wise search on a grid. In their direct search method, two kinds of multi-dimensional steps on the Φ surface are defined—an exploratory step which, when successful is followed by a pattern step. For the former, the unknown parameters are varied individually while for the latter, the parameters are all changed simultaneously. Exploratory steps proceed as follows. The objective function

is evaluated at the location of the initial guess $\vec{x}^{(0)} = (x_1^{(0)}, x_2^{(0)}, \dots, x_n^{(0)})$ and the result stored. Using a prescribed step size for x_1 , i.e. Δ_1 , the parameter $x_1^{(0)}$ is increased to $x_1^{(0)} + \Delta_1$ and the objective function evaluated. Should this lead to a reduction in the objective function, $x_1^{(0)}$ is replaced by $x_1' = x_1^{(0)} + \Delta_1$ so that the new guess point becomes $(x_1', x_2^{(0)}, \dots, x_n^{(0)})$ and the same procedure is followed for $x_2^{(0)}$, using Δ_2 , the prescribed step size for x_2 . If, on the other hand, replacing $x_1^{(0)}$ by $x_1^{(0)} + \Delta$ does not reduce the objective function, a change of direction is attempted, i.e. $x_1^{(0)} - \Delta_1$ is tried in place of $x_1^{(0)}$. When this too does not lead to a reduction in ϕ , Δ_1 is replaced by $\alpha\Delta_1$ ($\alpha < 1$) and the process is repeated from the start. This is continued, each new Δ_1 being decreased when there is no success, until there is either a decrease in the objective function for some value of Δ_1 or until Δ_1 becomes smaller than a preassigned limit. In either case, the same process is carried over to x_2 . In the former case x_1 is changed by the current value of Δ_1 in the direction indicated by the decrease in ϕ while in the latter case $x_1^{(0)}$ is used as x_1' and the guess point is therefore not changed. This process is applied to each parameter in turn until each of x_1, \dots, x_n has been varied. There are now two possibilities - either the new guess point $\vec{x}_1' = (x_1', \dots, x_n')$ is identical with the initial guess point $\vec{x}^{(0)} = (x_1^{(0)}, \dots, x_n^{(0)})$ or these two points differ in at least one parameter. In the former case, the surface minimum has probably been reached. At this point a proper test for solution is made to see if, indeed, the surface minimum has been reached. When \vec{x}_1' differs from $\vec{x}^{(0)}$ in at least one parameter a change vector $\vec{x}^{(1)} - \vec{x}^{(0)} = \vec{\Delta}_0$ has been determined which, when drawn from the initial guess point $\vec{x}^{(0)}$ points in the general direction of the minimum. Hooke and Jeeves suggest that, on the average, this change vector indicates the direction to the minimum sufficiently well enough for the objective function to be still smaller at $\vec{x}^{(2)} = \vec{x}^{(1)} + \vec{\Delta}_0$. The step $\vec{x}^{(2)} = \vec{x}^{(1)} + \vec{\Delta}_0$ is called a pattern step. Of particular importance is the fact that all parameters are varied simultaneously in a pattern step whereas in an exploratory step each of the n parameters is varied at least once. The time required for a complete exploratory step for n unknowns can obviously be much more than n times than required for a pattern step. Hooke and Jeeves choose to restrict themselves to one pattern step after a successful exploratory step. They then follow this single pattern step by a new exploratory step. Clearly, one might modify their method by making the number of consecutive pattern steps after a successful exploratory step a variable or even by continuing with pattern steps until there ceases to be a reduction in the objective function.

A number of further variants of the pattern search method are possible. One might, for example, choose to vary each component step of the exploratory phase from the original guess point $\vec{x}^{(0)}$ so that $\vec{x}^{(1)} = \vec{x}^{(0)} + \vec{\Delta}$ where $\vec{\Delta} = (\Delta_1, \Delta_2, \dots, \Delta_n)$ as calculated. This does not hold for the method as we have outlined it above since each component x_i is changed on a successful decrease in ϕ .

Thus, in other words, $\vec{\Delta}_p \neq \vec{\Delta}$. One might, furthermore, devise variations on the pattern step itself by replacing the vector $\vec{\Delta}$ as determined by the exploratory step by a different change vector $\vec{\Delta}_p$ for use in the pattern step. One might, for example determine $\vec{\Delta}_p$ as some kind of average over the $\vec{\Delta}_p$ vectors used in several of the preceding pattern steps or one might simply take a fraction of $\vec{\Delta}_p$.

Another approach which, according to our definition, can be included among the direct search methods is actually an independent parameter version of a variation on the secant approximation to the Newton-Raphson method. The method is also referred to as the Wegstein method.^{44,45} The basic algorithm for one dimension, is available among the basic library routines at many computer installations. The method has been used extensively by the author and his collaborators in the production of thermodynamic tables of atmospheric gases.⁴⁶ This method has been found to produce rapid convergence even when the initial guess values differ from the answers by more than factors of 10^{+6} or 10^{-6} . When coupled with a method for automatically converting from one set of reference species to another, where necessary, the method should produce rapid convergence entirely independent of initial guesses and should therefore be a truly automatic approach. We shall describe the method in some detail in one dimension but shall not specifically relate it to the actual Newton-Raphson method. The extension to multi-dimensional problems in the independent parameter approximation will then be shown to be straightforward.

This method can best be described in terms of the iteration (34). It should be noted that (34) can also be applied to the solution of equations of the form $\psi(\vec{x}) = 0$ since one can take $\Gamma(\vec{x})$ in the form

$$\Gamma(\vec{x}^{(k)}) = \vec{x}^{(k)} + \alpha \psi(\vec{x}^{(k)}),$$

where α is non-zero. With this form for $\Gamma(\vec{x})$, (34) reduces to the identity $\vec{x}^{(k+1)} = \vec{x}^{(k)}$ at the solution where $\psi(\vec{x}^{(k)}) = 0$. In the Wegstein method, which we shall describe in one dimension, (34) is modified by superimposing on it an in-out averaging algorithm. Thus, rather than take $\vec{x}^{(k+1)}$ as given by (34) for the next guess, an average between the value $\vec{x}^{(k)}$ into the iteration and $\vec{x}^{(k+1)}$ out of the iteration is taken to obtain as the next guess

$$\vec{x}^{(k+1)} = \vec{x}^{(k+1)} - q(\vec{x}^{(k+1)} - \vec{x}^{(k)}) \quad (38)$$

This produces a value given by $\vec{x}^{(k+1)}$ as calculated in (34) minus a fraction q of the calculated change between $\vec{x}^{(k)}$ and $\vec{x}^{(k+1)}$. It is easy to show that, in the secant approximation, $q = \frac{-m}{m-1}$ where m is the slope of the secant between $\vec{x}^{(k-1)}$ and $\vec{x}^{(k)}$. This enables q to be calculated at each iteration step. We are, however, much more interested in the advantages of using q as a fixed empirical quantity.

The use of (34) by itself will lead to one of the following behavior patterns for successive values of $\vec{x}^{(k)}$, (i.e. as functions of k the iteration number),

1. The values of $x^{(k)}$ oscillate and converge.
2. The values of $x^{(k)}$ oscillate and diverge.
3. The values of $x^{(k)}$ converge monotonically.
4. The values of $x^{(k)}$ diverge monotonically.

It is also possible for the character of the behavior pattern to change as n progresses. Generally, however, one particular kind of behavior should predominate. Each of the above behavior patterns for (34) can be improved through the use of (38) with fixed q in the sense that convergence can be speeded up. This can be done, in each case, by means of q values in the following ranges.

- | | |
|----------------------------|---------------|
| 1. Oscillatory convergence | $0 < q < 0.5$ |
| 2. Oscillatory divergence | $.5 < q < 1.$ |
| 3. Monotonic convergence | $q < 0$ |
| 4. Monotonic divergence | $q > 1$ |

The reason, in each case, follows from the use of q in (38) as an in-out averaging parameter. Thus, for the case where successive values oscillate with a trend toward the answer superimposed on this oscillation, it is clear that $x^{(k+2)}$ will lie between $x^{(k)}$ and $x^{(k+1)}$. This is what is meant by oscillation. Each value will, however, on the average be closer to $x^{(k+1)}$ than to $x^{(k)}$. This, in turn, is what is meant by convergence. Thus q must be so chosen that $\bar{x}^{(k+1)}$ lies between $x^{(k)}$ and $x^{(k+1)}$ but closer to $x^{(k+1)}$ than to $x^{(k)}$. This, in turn, is what is meant by convergence. Thus q must be so chosen that $\bar{x}^{(k+1)}$ lies between $x^{(k)}$ and $x^{(k+1)}$ but closer to $x^{(k+1)}$. This is clearly the case only for $0 < q < 0.5$. Examination of the other ranges listed for q values, shows them also to be designed to produce values of $\bar{x}^{(k+1)}$ in the general direction of the solution from $x^{(k+1)}$. Wegstein, with several examples, illustrates the damping effect this method has on oscillations, its ability to change divergent behavior into convergent behavior, and even to speed up convergence where there is monotonic convergence. It should be noted that $q = 1.0$ causes the iteration averaging scheme (38) to become $\bar{x}^{(k+1)} = x^{(k)}$ which destroys the ability to change x from one iteration to the next and hence causes a false locking in on an answer.

The extension of the Wegstein method to multi-dimensional problems is particularly simple. It is merely necessary to state such problems in such a way that the search method can be independently applied to each variable. In an approach used extensively by the author and his collaborators⁴⁶, n equations (38) were written, one being written for each variable with each equation having its own q parameter. In this approach, the algorithm

$$c_j^{(k+1)} = \frac{x_j}{\sum_{i=1}^l v_{ij} c_i^{(k)}} c_j^{(k)} \quad j = 1, \dots, c-1 \quad (39a)$$

was taken for (34) for all species except the electrons, the superscripts referring to iteration number. A different scheme had to be used for the electrons since for them $\chi_j = 0$. The algorithm

$$C_j^{(k+1)} = - \sum_{i=1}^{l-1} t_{ij} C_i^{(k)} \quad j = e \quad (39b)$$

was taken for the electrons, the sum extending over all species except the electrons themselves. It should be noted that, according to our definitions, t_{jj} for $j=e$ is positive for negative ions and negative for positive ions so that the former subtract from the sum while the latter add to it as required. Also note that (39b) is merely (20) for the electrons with $\chi_j=0$.

The iteration process proceeds as follows. Initial guesses for the concentrations of the reference species are substituted into (19) thereby producing initial guesses for the derived species. The method has been found to be sufficiently independent of these initial guesses for the reference species to allow the same set of initial guesses to be used for all problems. The initial guesses thus calculated for the derived species are substituted into (39a) and (39b) yielding interim new guesses for the reference species. These are then substituted into (38) and new guesses obtained for the reference species. These are used in (19) to start the next iteration. This process is continued until the proper criterion for solution is satisfied. It should be noted that, according to (20)

$$\frac{\chi_j}{\sum_{i=1}^l v_{ij} C_i} = 1$$

at the solution in which case (39a) becomes $C_j^{(k+1)} = C_j^{(k)}$ as required.

For the various systems studied by the author and his collaborators, the search method was found to be insensitive to the choice of each of the q_j except for a small sensitivity associated with the q_e of the electron concentration. This lack of sensitivity, particularly for the atomic species, persisted over an extremely large range of conditions. These included temperatures and densities for which the reference species were present in trace amounts with the major constituents being molecular species, those for which the reference species dominated, as well as those for which the reference species were again present in trace amounts with atomic ions being the main species. In all such cases the value $q_j = 0.5$ was used for all atomic reference species.

The electron concentration behaved somewhat differently as a function of iteration number, as might have been expected since (39b) is of quite a different form than is (39a). For the electron concentration, there tended to be oscillatory divergence with $q \approx 0.8$ being required. Somewhat more

rapid convergence was obtained by starting each problem with $q = 0.5$ for the electron concentration and increasing the value of q slightly with each iteration so as to reach $q \approx 0.8$ after a small number of iterations. It is important to point out that this scheme (i.e., $q = 0.5$ for all species except the electrons and a slowly increasing q value for the latter) once adopted was never modified regardless of the chemical system studied.

A number of precautions, common to iteration methods had to be taken. A ceiling was placed on the relative magnitude by which the C_j were allowed to change in one iteration. Thus, for

$$\frac{|C_j^{(k+1)} - C_j^{(k)}|}{C_j^{(k)}} > 100 \text{ or } < \frac{1}{100} \text{ the algorithms}$$

$$C_j^{(k+1)} = 100 C_j^{(k)} \text{ and } C_j^{(k+1)} = \frac{C_j^{(k)}}{100} \text{ were used.}$$

In practice these restrictions were found to operate only for current guess points quite far removed from the solution. These ceilings in effect guide the iteration point into the neighborhood of the solution. They play an important role in making the problem independent of the initial guess values as they undoubtedly also would if applied to other search methods.

REFERENCES

The number of articles and books listed among the references is meant to be extensive and sufficient for most purposes but is not meant to be exhaustive. They should, however, present an excellent starting point for anyone interested in compiling an exhaustive list of works on problems associated with the calculation of the thermodynamic properties and compositions of chemically reacting mixtures. The lists can be expanded considerably merely by adding items contained as references in the members of the list but which are not included in the list itself.

Certain of the technical reports listed below are available from central sources. These are the following:

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B. Reports with numbers preceded by the letters AD are available either from DDC, Headquarters, Cameron Station, 5010 Duke Street, Building 5, Alexandria, Virginia 22314, or The Clearing House for Federal Scientific and Technical Information (CFSTI), Springfield, Virginia 22151.

C. Reports with numbers preceded by the letters PB are available from CFSTI, Springfield, Virginia 22151.

D. Reports with the letters NACA or NASA along with the designated number are available either from the indicated source or from, The NASA Scientific and Technical Information Facility, P. O. Box 33, College Park, Md. 20740.

E. All other reports should be requested either from the publication office of the originating agency or, by author, title and number from CFSTI, Springfield, Virginia 22151.

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APPENDIX I

ILLUSTRATIONS OF THE MATRICES ASSOCIATED WITH THE STOICHIOMETRY OF REACTING GASEOUS MIXTURES

A number of matrices having to do with the stoichiometry of coupled chemical reactions in gaseous mixtures have been defined in the text. A complete understanding of these matrices and of their relationships to the chemistry of coupled chemical reactions is absolutely essential here. Without such an understanding, much of what appears in this chapter becomes unintelligible. For this reason, we include in this Appendix the matrices associated with a typical set of coupled reactions. We have purposely chosen a set of reactions which include electron attachment and detachment (i.e., ionization) in order to illustrate our treatment of the electron as a reference species. This treatment differs, in some respects, from standard chemical treatments, particularly with regard to notation.

The set of reactions with which we shall be concerned in this Appendix are reactions among the following thirteen species: N_2 , O_2 , N_2O , NO_2 , N^+ , O^+ , O_2^+ , O_2^- , N^{++} , O^{++} , N , O , and e^- , where e^- refers to the electron. Equation (1) of the text requires these to be written N_2 , O_2 , N_2O , NO_2 , Ne_{-1}^- , Oe_{-1}^- , $O_2e_{-1}^-$, $O_2e_{+1}^-$, Ne_{-2}^- , Oe_{-2}^- , N , O , and e^- , where a negative subscript for the electron indicates the absence of an electron and a positive subscript the presence of an extra electron. It should be noted that our notation differs from standard notation only in that the usual practice of writing ionic charge as a superscript on the chemical symbol has been replaced by specific reference to the presence or absence of the electron treated as a chemical species.

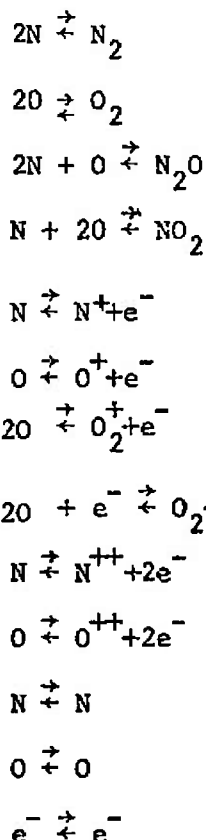
This notation leads to the following v_{ij} matrix elements.

REFERENCE SPECIES

Species	N	O	e ⁻
N ₂	2		
O ₂		2	
N ₂ O	2	1	
NO ₂	1	2	
Ne ₋₁ ⁻ (N ⁺)	1		-1
Oe ₋₁ ⁻ (O ⁺)		1	-1
O ₂ e ₋₁ ⁻ (O ₂ ⁺)		2	-1
O ₂ e ₊₁ ⁻ (O ₂ ⁻)		2	1
Ne ₋₂ ⁻ (N ⁺⁺)	1		-2
Oe ₋₂ ⁻ (O ⁺⁺)		1	-2
N	1		
O		1	
e ⁻			1

It should be pointed out that this set of v_{ij} matrix elements is associated with the chemical symbols of the various species and so is permanently associated with these species, regardless of the definition of reference species. The elements of the various T matrices, on the other hand, depend very strongly on the choice of reference species.

According to usual practice and notation, the chemical reactions to which we shall restrict this discussion might be written, with atoms and the electron as reference species

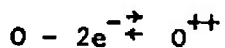
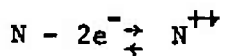
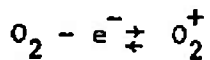
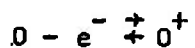
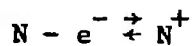


The T matrix associated with equation (5) of the text was a square matrix and included both a row and a column for each species. The reactions above define such a matrix as follows.

	N ₂	O ₂	N ₂ O	NO ₂	N ⁺	O ⁺	O ₂ ⁺	O ₂ ⁻	N ⁺⁺	O ⁺⁺	N	O	e ⁻
N ₂	1										-2		
O ₂		1									-2		
N ₂ O			1								-2	-1	
NO ₂				1							-1	-2	
N ⁺					1						-1		1
O ⁺						1					-1		1
O ₂ ⁺							1				-2		1
O ₂ ⁻								1			-2	-1	
N ⁺⁺									1		-1		2
O ⁺⁺										1	-1		2
N											1		
O												1	
e ⁻													1

where a blank position is used to indicate a zero matrix elements.

Somewhat better symmetry can be obtained, in the sense that reference species always appear on the same side of the equation, if the ionization reactions are written



It should be noted that this has no effect on the matrix element t_{ij} .

The second form of the \underline{T} matrix defined in the text uses the fact that the column under a derived species contains an entry only for the row associated with that same derived species, with that entry always being +1. With this +1 understood (and, more important, supplied when needed) the \underline{T} matrix can be written in terms of the reference species only. This results in the following matrix.

	N	O	e ⁻
N ₂	-2		
O ₂		-2	
N ₂ O	-2	-1	
NO ₂	-1	-2	
N ⁺	-1		1
O ⁺		-1	1
O ₂ ⁺		-2	1
O ₂ ⁻		-2	-1
N ⁺⁺	-1		2
O ⁺⁺		-1	2
N	1		
O		1	
e ⁻			1

It should be noted that, because atoms and the electron are used as reference species, these matrix elements correspond exactly to the v_{ij} . That this is not so for other choices of reference species is obvious on examination of the matrix elements in the text in the discussion of the matrix manipulations required for transformation of reference species. As stated above, such manipulations do not affect the v_{ij} .

APPENDIX II

THE INTRODUCTION OF REAL GAS EFFECTS

The expressions derived for the calculation of the species concentrations and those developed for the calculation of the properties of the mixture need to be modified to include real gas effects. In principle, these modifications should include both "internal" effects, i.e. modifications of the internal energy levels of individual species and "external" effects, i.e. those due to interactions between particles. For particle densities of interest here, however, changes in the internal energy levels of individual species will be negligible. As a result, the thermodynamic properties of individual species can be written as the sum of an ideal gas part (calculated as indicated in the text) and a part due to particle interactions involving the species. In this appendix we shall be concerned with the development of certain correction terms to the ideal gas expressions developed in the text.

According to the formalism developed for the ideal gas, the inclusion of expressions for the species activity coefficients will automatically extend the calculations of the species concentrations to include real gas effects. Such expressions need to be included in equation (10) for the free energy minimization method and in (17a) for the equilibrium constant method. The extension of the calculation of the thermodynamic properties of the mixture to include real gases is then completed on adding to the relations (23) a set developed for the mixture properties of an ideal gas appropriate terms for real gas effects and using, in the resulting expressions, concentrations calculated using real gas activity coefficients.

I. Real Gas Effects on the Calculation of the Species Concentrations

The chemical potential of a species in a gas mixture can be written

$$\frac{\mu_i(T, P, \vec{x})}{RT} = \frac{\mu_i^0(T)}{RT} + \ln P + \ln x_i + \sum (\Delta_k \mu_i) / RT$$

where \vec{x} indicates a dependence on the concentrations of all species and where each $\Delta_k \mu$ is a different additive effect. An activity coefficient can be defined for each of these effects through the relation

$$\ln \gamma^{(k)} = \Delta_k \mu / RT$$

leading to an expression for the chemical potential

$$\frac{\mu_i(T, P, \vec{x})}{RT} = \frac{\mu_i^0(T)}{RT} + \ln P + \ln x_i + \ln \left[\prod_k \gamma_i^{(k)} \right]$$

The expression (10) on which the calculation of the concentrations in the free energy minimization method is based then need only be modified by taking

$\gamma_i = \prod_k \gamma_i^{(k)}$ including as many of the k effects as desired. The modification

of (17a) is equally straight forward merely requiring the definition of a γ^i for each of the k effects. It should be noted that these effects can include such diverse items as quantum effects, higher virial coefficients, etc. In short, the formalism includes all effects which produce additive terms in the chemical potential.

The effect of second virial coefficients can be included immediately on writing down the appropriate correction to the chemical potential. Thus

$$\frac{\Delta \mu_i}{RT} = \frac{2}{V} \sum_{k=1}^L C_k B_{ik} \quad (B1)$$

$$\text{so that } \ln \gamma_i = \frac{2}{V} \sum_{k=1}^L C_k B_{ik}$$

This can be substituted directly into (10) for the free energy minimization method. For the equilibrium constant method, it is necessary to calculate

$$\gamma_i^1 = \left[\prod_j \gamma_j^{v_{ij}} \right] / \gamma_i$$

for the i^{th} chemical reaction. Thus

$$\gamma_i^1 = \exp \left[\frac{2}{V} \sum_{k=1}^L C_k B_{ik} \right]$$

so that

$$\frac{\prod_j \gamma_j^{v_{ij}}}{\gamma_i} = \exp \left[\frac{2}{V} \sum_i v_{ij} \sum_{k=1}^L C_k B_{ik} - \frac{2}{V} \sum_{k=1}^L C_k B_{jk} \right]$$

$$\text{and } \gamma_i' = \exp \left[\frac{2}{V_0} \rho/\rho_0 \sum_j v_{ij} \sum_{k=1}^L C_k B_{ik} - \frac{2}{V_0} \rho/\rho_0 \sum_{k=1}^L C_k B_{ik} \right] \quad (\text{B2})$$

where V_0 is the volume of one mole at standard conditions. It should be noted that this γ_i' should be substituted into (19) as a factor multiplying \bar{k}_i .

The limiting law Debye-Huckel correction to the calculation of the species concentrations can also be included in a straightforward manner. In this case

$$\frac{\Delta\mu_i}{RT} = \frac{-\pi^{1/2} \left(\sum_s Z_s^2 C_s \right)^{1/2}}{(DkT)^{3/2}} \left(\rho/\rho_0 \right)^{1/2} \left(\frac{N_0}{V_0} \right)^{1/2} Z_i^2$$

where N_0 is the number of particles per mole at standard conditions, V_0 the corresponding volume, D the dielectric constant of the mixture and Z_s the ionic charge of each ion of type s . It follows then that

$$\ln \gamma_i = \left[-\frac{\pi^{1/2}}{(DkT)^{3/2}} \left(\rho/\rho_0 \right)^{1/2} \left(\frac{N_0}{V_0} \right)^{1/2} Z_i^2 \left(\sum_s Z_s^2 C_s \right)^{1/2} \right] \quad (\text{B3})$$

Substitution of this expression into (10) guarantees the inclusion of the limiting law Debye-Huckel correction. In the equilibrium constant method, this correction is inserted by means of the additional factor

$$\gamma_i' = \frac{\pi \gamma_j^{v_{ij}}}{\gamma_i} = \exp \left[-\frac{\pi^{1/2}}{(DkT)^{3/2}} \left(\rho/\rho_0 \right)^{1/2} \left(\frac{N_0}{V_0} \right)^{1/2} \left(\sum_s Z_s^2 C_s \right)^{1/2} \left(\sum_j v_{ij} Z_j^2 - Z_i^2 \right) \right] \quad (\text{B4})$$

Where the reactions are written in terms of complete ionization to ions and electrons, this can be simplified slightly by making use of the identity

$$\sum_i v_{ij} Z_i^2 = Z_j$$

for that case. This follows from the fact that for such reactions $v_{ij} = 0$ except for the electrons while for the electrons $v_{ij} = -Z_j$, the ionic^{ij} valence and $Z_i = 1$ the electronic valence.

Woolley has developed additional corrections for various other effects including third virial coefficients, the detailed calculation of the dielectric constant and the finiteness of the ionic core.

At this point, the advantages of the direct search method should become apparent. We have defined direct search methods to include all those for which only the objective function needs to be evaluated. The addition of γ_j^i factors in (17a) as complex as (B2) and (B4) or of \ln_j^i terms in (10) of the complexity of (B1) and (B3) would require much more complex reprogramming in methods involving the use of derivatives than is required in methods for which only the objective function is evaluated. Furthermore, the former requires some additional mathematical analysis in these cases whereas the latter approach does not.

II. Real Gas Effects on the Calculation of the Properties of the Mixture

In part I of this appendix, we showed how the species concentrations can be calculated including various real gas effects. These are the concentrations which must now be used in the expressions for the thermodynamic properties of the mixture in terms of the appropriate properties of the individual species. These expressions, however, are not simply those derived in the text for the ideal gas mixture. In addition to these ideal gas terms there must be included terms which specifically refer to the real gas effects on the properties themselves. Thus, the compressibility factor must now be written

$$Z = \frac{PV}{RT} = Z^* + \sum_k \Delta_k Z$$

where Z^* is the ideal gas value, i.e. $Z^* = \sum_{i=1}^L C_i$ and the $\Delta_k Z$ are expressions for the various real gas effects. Thus, for the effect of the second virial coefficient

$$\Delta Z = \frac{1}{V_0} \rho / \rho_0 \sum_{\alpha=1}^L \sum_{\beta=1}^L C_{\alpha} C_{\beta} B_{\alpha\beta} \quad (B5)$$

where $B_{\alpha\beta}$ is the second virial coefficient which describes the interaction between species α and species β . For the limiting law Debye-Huckel effect

$$\Delta Z = \frac{-\pi^{1/2}}{3} \frac{\epsilon^3}{(DkT)^{3/2}} \left(\rho/\rho_o \right)^{3/2} \left(\sum_{\alpha=1}^L Z_{\alpha}^2 C_{\alpha} \right)^{3/2} \left(\frac{N_o}{V_o} \right)^{1/2} \quad (B6)$$

where Z_{α} is the ionic charge of species α .

The internal energy needs now to be computed using

$$\frac{E}{RT} = \frac{E^*}{RT} + \sum_k \Delta_k \left(\frac{E_k}{RT} \right)$$

where E^* is the ideal gas value and, for the effect of the second virial coefficient,

$$\Delta \frac{E}{RT} = \frac{-1}{V_o} \left(\rho/\rho_o \right) \sum_{\alpha=1}^L \sum_{\beta=1}^L C_{\alpha} C_{\beta} T \frac{dB_{\alpha\beta}}{dT} \quad (B7)$$

While for the Debye-Huckel effect, the correction for the internal energy is three times (B6), i.e. three times that for the compressibility factor. The entropy is to be calculated from

$$\frac{S}{R} = \frac{S^*}{R} + \sum_k \Delta_k \left(\frac{S_k}{R} \right)$$

where S^* is the ideal gas value where the second virial effect is given by

$$\Delta \frac{S}{R} = -\frac{1}{V_o} \left(\rho/\rho_o \right) \sum_{\alpha=1}^L \sum_{\beta=1}^L \left[C_{\alpha} C_{\beta} B_{\alpha\beta} + T \frac{dB_{\alpha\beta}}{dT} \right] \quad (B8)$$

and the Debye-Huckel limiting law effect is given by (B6).

Corrections are easily derived for the various properties which depend on derivatives of these properties by differentiation of (B5) - (B8) as required.

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